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The Kinetics and Mechanism of the Reaction Between Carbon-Disulfide and Bis-(Para-Methoxyphenyl)methyleneimine.

Kenneth Norman Yarbrough

Louisiana State University and Agricultural & Mechanical College

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THE KINETICS AND MECHANISM OF THE REACTION
BETWEEN CARBON DISULFIDE AND
BIS-(p-METHOXYPHENYL)METHYLENEIMINE

A Dissertation

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy

in

The Department of Chemistry

by

Kenneth Norman Yarbrough
B.S., North Texas State University, 1953
M.S., North Texas State University, 1954
August, 1965

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ABSTRACT

The reaction between carbon disulfide and bis-(p-methoxyphenyl)methyleneimine was studied at 40°C, 50°C, and 60°C. Dilute solutions of the imine in carbon disulfide were studied both in the absence and presence of copper metal, and copper was shown to react and go into solution in the system. Copper was excluded throughout most of the study. More concentrated solutions of imine in bromoform with slight excesses of carbon disulfide were allowed to react in sealed glass tubes at controlled temperatures.

Concentrations of imine remaining and final products formed at selected times were determined on solutions of the reaction mixtures in carbon disulfide. The final products were 4,4'-dimethoxythiobenzophenone and bis-(p-methoxyphenyl)methyleneiminium thiocyanate. The imine concentration was determined by its characteristic absorption in the infrared at 887 cm^{-1} . The thioketone was determined by its characteristic absorption at $593\text{ m}\mu$. The total iminium thiocyanate concentration was obtained by summing the weight of salt as precipitated crystals in excess carbon disulfide and the salt determined as CNS^- extracted from the saturated solution containing the crystals. The absorption at $461\text{ m}\mu$ of the Fe (III) complex was used to determine CNS^- .

The N-proton peak in the nuclear magnetic resonance spectrum of the imine was observed to move markedly downfield as the reaction progressed. A rapid proton exchange between $=\text{N}-\text{H}$ and $=\text{N}\begin{smallmatrix} \text{H} \\ \text{H} \end{smallmatrix}\oplus$ was proposed to explain

the downfield motion of the single peak. The two component system, imine plus iminium thiocyanate, was used to verify that the N-proton peak position was a function of relative concentrations of $=N-H$ and $=N\begin{smallmatrix} H \\ \diagup \diagdown \\ H \end{smallmatrix}\oplus$. Study of other systems indicated lability of the imine N-proton and its rather complete exchange with other labile protons. The N-proton peak positions observed in kinetic runs were only partially accounted for by the amount of iminium thiocyanate present. The presence of $=N\begin{smallmatrix} H \\ \diagup \diagdown \\ H \end{smallmatrix}\oplus$ in excess of that as iminium thiocyanate perhaps could have accounted for the observed shifts.

At 40°C the amount of imine disappeared was balanced, within experimental error, by the amounts of thioketone and iminium thiocyanate formed throughout the reaction time. A similar materials balance was also obtained late in the reactions at 50°C and 60°C, but early in reactions at these temperatures, more imine had disappeared than could be accounted for in the formation of thioketone and iminium thiocyanate. At all three temperatures thioketone and iminium thiocyanate were simultaneously produced in equal molar amounts.

The mechanism proposed for the reaction between carbon disulfide and bis-(p-methoxyphenyl)methyleneimine consisted of several consecutive reactions. Carbon disulfide and imine were assumed to form a dithiocarbamic acid which rapidly attacked imine to form the iminium dithiocarbamate. The dithiocarbamate ion underwent rearrangement through internal nucleophilic attack and subsequently decomposed to

CHAPTER I

INTRODUCTION AND HISTORICAL APPROACH

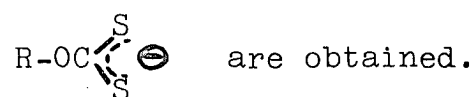
The reaction of elemental sulfur with N-(4,4'-dimethoxybenzohydrilidene)benzylamine, $(\text{CH}_3\text{OC}_6\text{H}_4)_2\text{C}=\text{N}-\text{CH}_2\text{C}_6\text{H}_5$, was reported by Schönberg and Urban (11) in 1934. It was adapted to a selective quantitative determination of elemental sulfur in the presence of other chemical forms of sulfur by Ory, Warren, and Williams (9). They showed that the reaction gave reproducible amounts of 4,4'-dimethoxythiobenzophenone, $(\text{CH}_3\text{OC}_6\text{H}_4)_2\text{C}=\text{S}$, under controlled conditions. The thioketone, an intensely blue compound, was easily determined by a characteristic absorption near 590 m μ . Neely and Williams (8) studied the infrared spectra of the reagent and known reaction products and were able to assign most of the observed bands to characteristic groups. In these studies hydrogen sulfide, benzonitrile, and 4,4'-dimethoxythiobenzophenone were identified as products. Huddleston (5) studied the rate of formation of these products and discovered a new acid soluble product which was later identified as bis(p-methoxyphenyl)methyleneimine by Williams, Koenig, Huddleston, Couvillon, and Castille (13). They found that the imine reacted with either hydrogen sulfide or carbon disulfide to form a blue compound, presumed to be the thioketone. Subsequent chromatographic separation of the blue product and comparison of its infrared spectrum with that of pure thioketone synthesized in these laboratories (12) confirmed their presumption.

The reaction between carbon disulfide and bis-(p-methoxyphenyl)methyleneimine offered interesting and unusual possibilities for further study and is, in fact, the basis for the kinetic and mechanism studies reported here.

Of special interest in this study was work of the type reported by Cotton and Wilkinson (1) and Feigl (3). Cotton and Wilkinson (1) point out that treatment of CS₂ with various primary or secondary amines in sodium hydroxide solution yields dithiocarbamates of general formula:

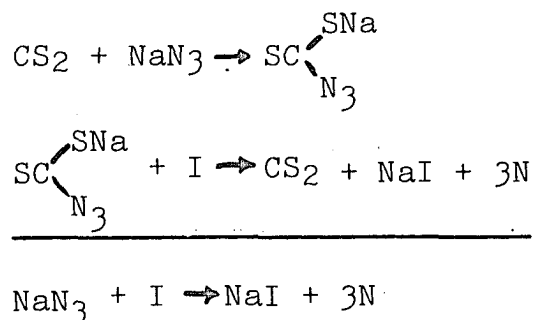


whereas, if sodium alkoxides are used instead of amines, xanthates of general formula:



The dithiocarbamate salts form a large number of metal complexes and are of great industrial importance as catalysts in the vulcanization of rubber.

Feigl (3) cites an interesting test for the C=S group as an accelerating catalyst for the iodine-sodium azide reaction:



Because of the large number of covalent states that both nitrogen and sulfur may exhibit, much diversity

was expected in studies of organo-nitrogen-sulfur systems. Results are quite often unpredictable and have led to widely different interpretations by various investigators. Therefore, it was desirable to make such studies in systems which gave well defined products and reproducible reactions under controlled conditions. The achievement of a reasonable materials balance was essential in this respect, and it will be shown that our system of carbon disulfide plus imine gave a reasonable materials balance of reproducible, well-characterized products.

CHAPTER II

EQUIPMENT, METHODS, AND MATERIALS

Equipment

Infrared spectra were obtained using a double beam Beckman IR-7 recording spectrophotometer. Spectra of solid materials were obtained from disks of potassium bromide containing a small amount of sample. The disks were prepared by grinding the KBr-sample mixture in a "Wigglebug" and pressing it in a Perkin-Elmer die. Spectra of solutions were obtained by use of rather well-matched sodium chloride cavity cells of 0.5 mm path length supplied by Barnes Engineering Company, Stamford, Connecticut. These cells are cut by ultrasonic methods and are not sold as matched pairs. It was fortunate that a matched pair allowing the baseline shown in Figure 4 was found in comparisons among four production line cells.

Visible spectra were obtained using a Beckman Model DB spectrophotometer with matched quartz cells of 1 cm path length.

Nuclear magnetic resonance spectra were obtained using a Varian Associates, Model HR-60, spectrometer. The data cited in Figure 14 were obtained prior to the installation of an external reference proton stabilization controller. Imine spectrum calibration was performed using a Varian Model A-60 instrument by Dr. W. L. Senn of Esso Research Labs, Baton Rouge, Louisiana. All other nuclear

magnetic resonance data reported here were obtained after installation of the proton stabilizer.

The reaction mixture temperature was controlled in the NMR experiments by bathing the reaction tube in a stream of nitrogen gas at constant temperature. The nitrogen was passed over a nichrome filament heater. Input to the heater was constant and nitrogen flow rate was held constant to effect a steady state system. A small, calibrated thermometer was spun in the NMR sample cavity and monitored for six to eight hours at each of the selected reaction temperatures. No variation in excess of 0.1°C from the selected temperature was observed. A Sargent constant temperature water bath was used in the other experiments. Similar monitoring with the same thermometer resulted in no observed variation in excess of 0.1°C .

Conductivity measurements were done using an Industrial Instruments, Inc., Model RC 16, conductivity bridge. The cell was of 50 ml volume with platinum electrodes and had a cell constant of 0.0140 cm^{-1} .

Ordinary volumetric glassware was used in all operations except reaction mixture preparation in which an "Agla" micrometer syringe (Burroughs, Wellcome, and Co., London) was used. The accuracy of this syringe was such that volumes as small as 0.01 ml could be measured to within $\pm 0.00005\text{ ml}$. All volumetric work was done at a temperature between 25 and 27°C .

Analytical weighing was done using a Mettler, type H6, balance under warranty inspection.

Methods

The reactions between carbon disulfide and bis-(p-methoxyphenyl)methyleneimine were carried out in sealed glass tubes of 5 mm inside diameter, 1 mm wall thickness, and 115 mm length. Approximately 0.282 g imine was weighed into each tube to which 0.8500 ml bromoform was added. Then 0.1500 ml carbon disulfide was carefully added with maintenance of an interface between the liquids. The tube was equilibrated with one gallon of dry nitrogen at 25°C and 1 atmosphere pressure and sealed with a torch. The sealed tubes were brought to reaction temperature with minimum disturbance of the interface. Each tube was vigorously shaken by hand for about 15 seconds and returned to the temperature bath. Reaction time was counted from the beginning of shaking. Each tube was quenched in ice-brine solution. Reaction time was considered stopped at placing the tube in the cold bath. Each reaction mixture was kept in a refrigerator freezer between handlings necessary in analyses.

The techniques used in obtaining the NMR data were similar to those above except as follows. Glass sample tubes supplied by Varian were used. They were thin-walled, 4 mm inside diameter, and 180 mm in length. Carbon disulfide at room temperature was added to a solution of imine in bromoform at the reaction temperature. The tube was sealed with a cork stopper, vigorously shaken, and placed in the thermostat in the NMR spectrometer. Reaction time was counted

from the time the tube was returned to the thermostat. No quenching was necessary, as the reaction was allowed to proceed in the instrument.

For each kinetic run a dozen reaction tubes were prepared. After quenching they were stored in a freezer and kept frozen until they could be analyzed. Each tube was warmed to room temperature, shaken, and broken. The contents were dissolved in 20 ml carbon disulfide and cooled to about 10°C in open beakers. Those samples in which crystals formed were filtered through weighed, fritted crucibles, with care to prevent the filtrate touching any material other than glass. The crystals were washed with CS₂, dried, and weighed as bis-(p-methoxyphenyl)methyleneiminium thiocyanate. The filtrate was diluted to 25.0 ml with CS₂ for the following analyses.

A portion of the filtrate was placed in the sodium chloride "sample" cavity cell and the infrared spectrum taken for imine analysis. A solvent mixture made by diluting 8.50 parts of bromoform to 250 parts with CS₂ was used in the "reference" cavity cells. Calibration details of this procedure are given in Chapter IV.

A portion of the filtrate was suitably diluted with CS₂ and the absorption at 593 m μ observed for analysis of 4,4'-dimethoxythiobenzophenone. Carbon disulfide was used in the reference cell. Calibration details of this procedure are given in Chapter IV.

A 10.00 ml portion of the filtrate was extracted with two 20 ml portions of 0.5% KOH. The aqueous phase was treated with 4.0 ml of 10% cadmium acetate solution and allowed to digest at room temperature for two hours. It was filtered and the precipitate was twice washed with water which was added to the filtrate. A 10.0 ml portion of a reagent prepared by dissolving 25.0 grams $\text{Fe}(\text{NO}_3)_3$ plus 25 ml concentrated HNO_3 in 500 ml was added to the filtrate. After waiting five minutes the absorption at 461 m μ was observed for analysis of dissolved CNS^- . Calibration details of this procedure are given in Chapter IV.

Materials

Bromoform was obtained from Eastman Organic Chemicals. It was vacuum distilled prior to use, stored in an amber glass bottle, and re-distilled at the appearance of discoloration.

Carbon disulfide, analytical reagent grade, was obtained from Mallinckrodt and used as received.

4,4'-Dimethoxythiobenzophenone, bis-(p-methoxyphenyl)methyleneimine, and its thiocyanate salt were synthesized in these laboratories according to the procedures discussed in the following chapter.

N-(4,4'-dimethoxybenzohydrilidene)benzylamine was obtained from K and K Laboratories and used as received.

4,4'-Dimethoxybenzophenone was obtained from both Eastman Organic Chemicals and K and K Laboratories and used as received.

CHAPTER III

SYNTHESES AND CHARACTERISTICS OF MATERIALS

4,4'-Dimethoxythiobenzophenone was prepared by refluxing 14.35 g (5.75×10^{-2} moles) of 4,4'-dimethoxybenzophenone with excess phosphorus pentasulfide in 250 ml of reagent-grade carbon tetrachloride for 30 hours. The solution was decanted, washed three times with 250-ml portions of saturated aqueous sodium carbonate followed by three 250-ml distilled water washes, and dried over anhydrous sodium carbonate. The carbon tetrachloride solution was chromatographed through an activated alumina column previously washed with carbon tetrachloride. Unreacted ketone was retained while thioketone was eluted. Center cuts of the thioketone fraction from several chromatograms were collected under nitrogen and stored in the dark. The solvent was evaporated at reduced pressure, and 6.0 g (2.3×10^{-2} moles) of crystalline 4,4'-dimethoxythiobenzophenone was obtained and stored under nitrogen in an amber glass bottle. Yield through all operations was 40%.

The very strong 1650 cm^{-1} carbonyl band of the ketone was absent in the spectrum of the thioketone. The melting point of the product, determined in a sealed capillary under one atmosphere of nitrogen (30°), was $116\text{--}117^{\circ}\text{C}$.

The synthesis and purification procedures reported here proved to be particularly convenient, because they minimized handling problems due to light sensitivity, air

oxidation, and thermal instability of the product. The purity of the thioketone described here seems the highest yet attained, and the compound analysis (Table I) is the most complete yet reported. The infrared spectrum of the thioketone is shown in Figure 1. Of particular interest are two absorption bands at 740 cm^{-1} and 1045 cm^{-1} which are newly assigned to carbon-sulfur bonding in the thioketone.

λ_{max} (visible) and molar extinction coefficients for this compound were determined in several solvents. The results of this work are given in Chapter IV.

TABLE I
Analyses of 4,4'-Dimethoxythiobenzophenone

Sample	C (%)	H (%)	O (%)	S (%)	m.p. (°)
Present work*	69.53 69.76	5.48 5.61	12.33 12.36	12.20 12.39	116-117
Gatterman (4)	-	-	-	-	115
Schönberg (10)	70.19	6.03	-	12.13	114-115
Losach (6)	-	-	-	-	116
Theoretical	69.74	5.46	12.39	12.41	-

*Analyses done by Galbraith Laboratories,
Knoxville, Tennessee

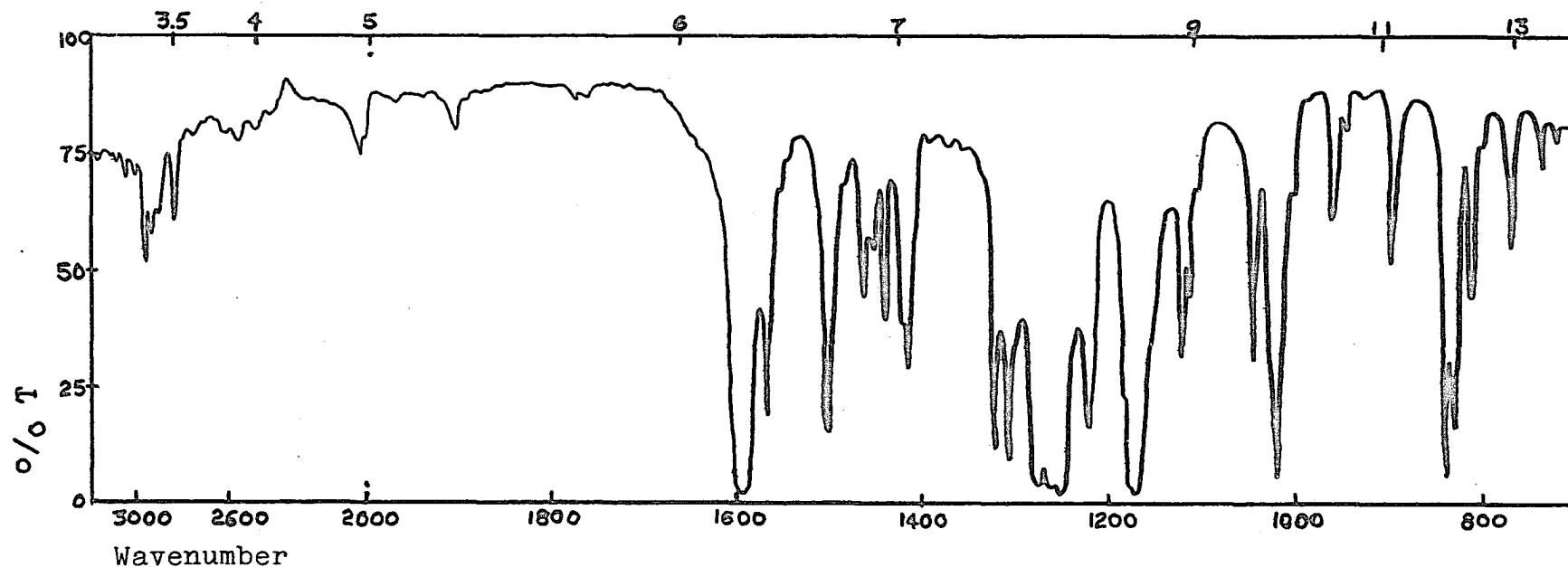


Figure 1. Infrared Spectrum of 4,4'-Dimethoxythiobenzophenone in KBr Disk

Comparison of the spectra of 4,4'-dimethoxythiobenzophenone (I), 4,4'-dimethoxybenzophenone (II), and bis-(p-methoxyphenyl)methyleneimine (III) shows 3 bands in I which are not in II nor III: 1221 cm^{-1} , 1045 cm^{-1} , and 740 cm^{-1} . The first 2 are strong bands, and the last is weak. Others (7,10) have reported the 1221 cm^{-1} band at 1224 and 1219 cm^{-1} and made the assignment to carbon-sulfur bonding. This study seems to verify that assignment and to indicate that the 1045 cm^{-1} and 740 cm^{-1} are also associated with carbon-sulfur bonding in aromatic thioketones.

Exposure of a potassium bromide disk containing 10^{-3} molar thioketone to high energy ultraviolet for one hour causes no noticeable change, while exposure of a 10^{-3} molar solution of the thioketone in various solvents to sunlight causes fading of the characteristic blue color in a few moments. Apparently the photochemical reaction involved is collision dependent.

A sample of solid thioketone stored in an amber bottle for sixteen months with occasional opening was examined by Dr. Rene Farhi using thin layer chromatography. In a private communication, he reported no impurities.

Donle and Volkert (2) evaluated the physical properties of several organic compounds including those of p,p'-dianisylthioketone, the thioketone of interest in this study. They measured the dipole moment and found it to be 4.44 debye compared to 3.90 debye for the corresponding ketone. The behavior of the absorption maxima and extinction coefficient in various solvents also indicates a greater polarity in the carbon-sulfur bond than in the carbon-oxygen bond.

Bis-(p-methoxyphenyl)methyleneimine was synthesized in these laboratories by several different methods. The reaction studied by Huddleston (5) was used. He found that Schonberg's reagent, N-(4,4'-dimethoxybenzohydrilidene)-benzylamine, reacts with elemental sulfur to yield 4,4'-dimethoxythiobenzophenone, benzonitrile, hydrogen sulfide, and other products. One of the other products was bis-(p-methoxyphenyl)methyleneimine (13), the imine of interest here.

Huddleston's work was further complicated by the rapid reaction between the imine and hydrogen sulfide to form the thioketone and other products. A materials balance for the reaction studied by Huddleston has not yet been achieved, because all products are not yet identified.

Schönberg's reagent was reacted with a slight excess of sulfur at 170°C for about ten minutes in a sealed tube. The reaction mixture was taken up in benzene, filtered, and dry hydrogen chloride was passed through it. Fine white crystals of the imine hydrochloride were recovered, washed with benzene, and dissolved in water. On making the aqueous solution slightly basic with NaOH, the imine came out of solution as a flocculant white solid. It was extracted into ether solution which was dried over anhydrous sodium carbonate. The ether was evaporated on a steam bath until imine crystals formed. Excess ether solution was decanted to another beaker for further evaporation and recovery of imine. The imine recovered here was slightly contaminated with 4,4'-dimethoxybenzophenone, but subsequent purification by methods later described gave a product of high purity. While this method of synthesis was fast and relatively simple, it gave low yields on the order of 5-10% from rather expensive starting material.

Another synthesis of the imine was done using a method cited by Williams, Koenig, Huddleston, Couvillon, and Castille (13). Reaction of p-methoxyphenylmagnesium bromide

with anisonitrile, followed by hydrolysis with 5% hydrochloric acid, gave a product, the melting point and infrared spectrum of which were identical with those of the material obtained from Schönberg's reagent and sulfur. On ignition this product gave an ash of about 6% by weight. The ash gave a positive magnesium test with p-nitrobenzene-azo-resorcinol. The product was also slightly contaminated with 4,4'-dimethoxybenzophenone. The yield of Grignard reagent was very high, according to the reaction of stoichiometric amounts of magnesium. However, the overall yield of imine was always low regardless of the order of addition of reactants. Low solubility of imine in 5% hydrochloric acid and hydrolysis of imine to ketone were responsible for some loss of product. Side reactions also contributed to preventing greater than 15% yields.

A high yield synthesis of the imine was accomplished by reacting the dichloride of 4,4'-dimethoxybenzophenone with sodamide in liquid ammonia. The yield was 95% of imine of 95% purity. Red crystals of the dichloride were obtained by refluxing 81 g of the ketone with 100 g thionyl chloride for 3 hours, letting it sit overnight, and vacuum distilling off excess thionyl chloride. The wet, red crystals of dichloride were dissolved in 500 ml chloroform and retained for later use. About 500 ml liquid ammonia was condensed in a 3-neck flask with a CO_2 -acetone filled Dewar condenser attached. A small amount, 0.2 g, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was added as a catalyst, and 15.3 g sodium in small pieces was added with stirring. More ammonia was condensed as necessary

to replace that lost by evaporation. After complete solution of the sodium, the 500 ml chloroform solution of dichloride was slowly added to the liquid ammonia solution. Extreme caution was practiced at this dangerous point. After addition was complete, the Dewar condenser was replaced with an ordinary ice water condenser, and the mixture was stirred at room temperature for two hours. The reaction mixture was filtered. The precipitate was washed with chloroform which was added to the filtrate. Dry hydrogen chloride was passed through the filtrate until filtrate dropped on wet p-Hydrion paper gave a pH of 6. Solid ammonium chloride was filtered out and the filtrate was concentrated to about 200 ml by passing dry nitrogen through it. To the 200 ml chloroform solution was added 800 ml ice cold ligroin. Imine crystallized rapidly. The imine obtained here was contaminated with ketone. The purification method discussed below gave pure imine.

Melting range and melting point were not sufficient criteria for purity of the imine. A sample of imine containing about 30% ketone had a melting range of 129-133°C. A sample of imine containing about 8% ketone had a melting range of 130.5-131.5°C. A sample of imine having no 1650 cm^{-1} ketone absorption had a melting range of 131.0-131.5°C. All melting points were determined in a capillary melting point apparatus.

The infrared spectra of potassium bromide disks of pure imine and imine-ketone mixture differed only in that the latter had an absorption at 1650 cm^{-1} .

Fractional crystallization, sublimation, and zone refining were attempted with no separation of the imine-ketone mixture. Difficulty of separation by these methods and the rather sharp melting point of the imine-ketone mixture indicated compound formation, possibly by hydrogen bonding. However, the carbonyl absorption peak of pure ketone was not noticeably shifted in the imine-ketone mixture.

Purification of the imine was accomplished by the following method. The details of the method were very important for successful results. Imine of about 92% purity was dissolved in ether to make a saturated solution at room temperature. The ether solution was extracted with three volumes of cold 5% HCl. Ice cold concentrated NaOH was added to the HCl solution to a pH of 5 while temperature of the mixture was not allowed to exceed 10°C. The solution was kept at 10°C for ten minutes and filtered. The filtrate was treated with more cold NaOH to a pH of 9 and extracted with ether as quickly as possible. The ether phase was dried over anhydrous sodium carbonate and evaporated with a stream of dry nitrogen. Complete evaporation was not practiced. Excess ether solution was decanted from imine crystals. The crystals were washed with a small portion of anhydrous ether. Imine purified in this manner gave the infrared spectrum shown in Figure 2. There was no absorption at 1650 cm^{-1} and the melting range of the imine was 131.0-131.5°C. About half of the imine was lost in this purification procedure. Elemental

analysis of the purified imine was:

found: C=74.51%, H=6.04%, N=5.59%

calculated for $C_{15}H_{15}NO_2$: C=74.63%, H=6.31%, N=5.80%.

Bis-(p-methoxyphenyl)methyleneiminium thiocyanate was prepared by reacting bis-(p-methoxyphenyl)methyleneimine with carbon disulfide. Much of the compound used in this study was recovered from reaction mixtures used in kinetic runs. It was recrystallized from bromoform by the addition of carbon disulfide. Elemental analysis of the purified salt was:

found: C=63.84, H=5.27, N=9.21, S=10.80

calculated for $C_{16}H_{16}N_2O_2S$: C=64.0, H=5.38, N=9.36, S=10.70.

The salt was found to be very slightly soluble in non-polar solvents and readily soluble in polar solvents. An aqueous solution of the compound gave a positive thiocyanate test with Fe (III). Recovery of imine from an aqueous solution of the salt was effected by making the solution slightly basic.

Long needles of the salt recovered from a solution of imine in carbon disulfide and washed with carbon disulfide gave the potassium bromide disk infrared spectrum shown in Figure 3. The melting range of the needles was 152-163°C with decomposition.

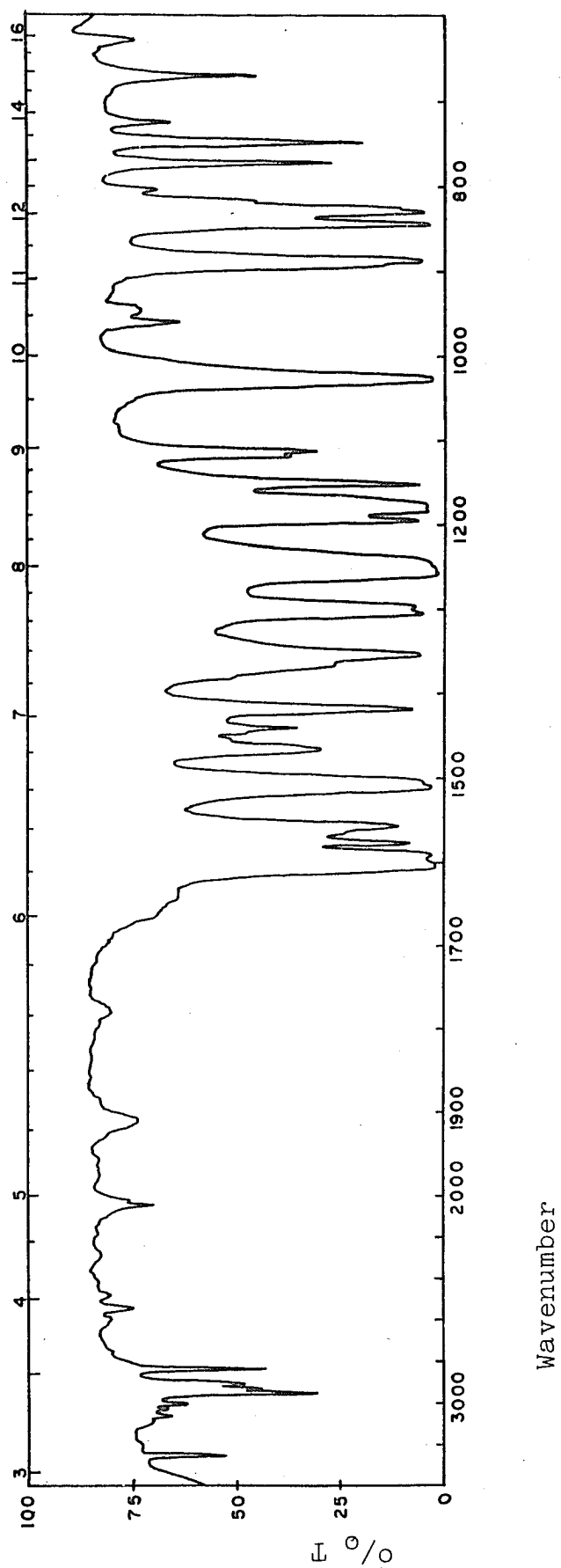


Figure 2. Infrared Spectrum of Bis-(p-methoxyphenyl)methyleneimine in KBr Disk

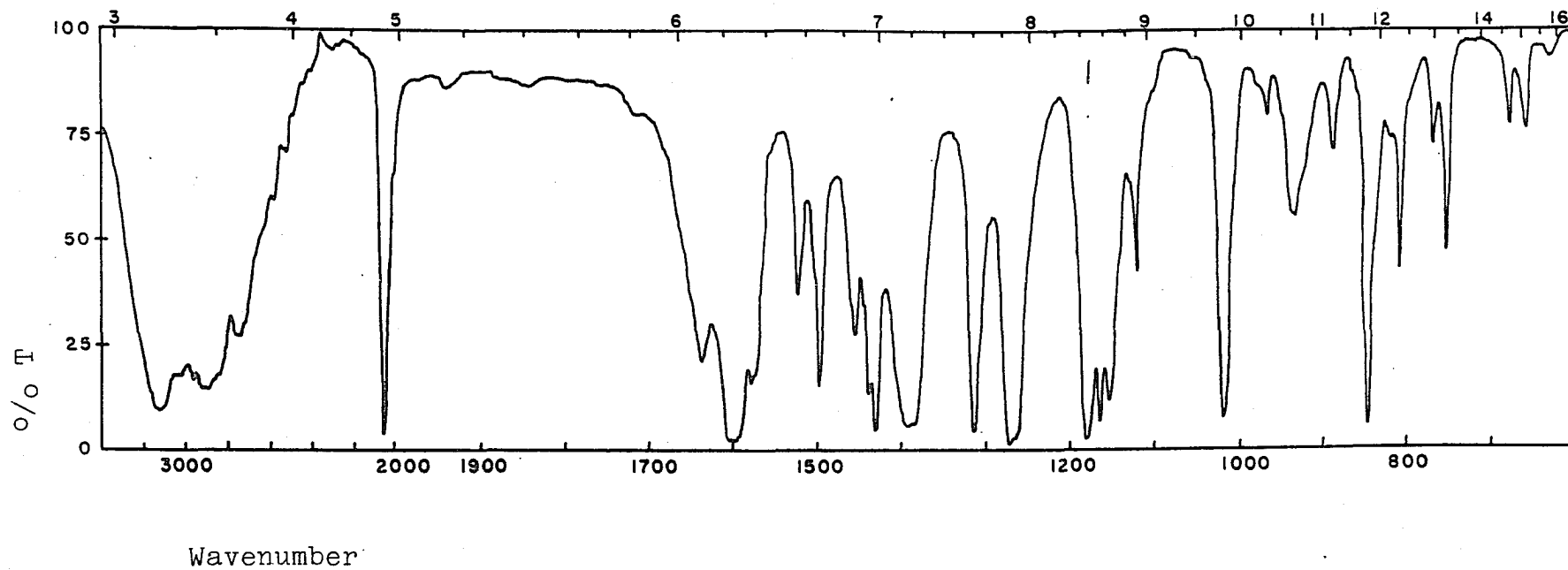


Figure 3. Infrared Spectrum of Bis-(p-methoxyphenyl)methyleneiminium thiocyanate in KBr Disk

CHAPTER IV

CALIBRATION DETAILS FOR ANALYSES

Solvent Selection

Bromoform was selected as a solvent for the reaction for several reasons. It was found to be transparent in the spectral regions of interest. The solubility of reactants and products was found to be high in bromoform and the single proton of bromoform made its nuclear magnetic resonance spectrum simple. The high boiling point of bromoform permitted heating of the reaction mixture over the temperature range studied without a significant increase in vapor pressure in the sealed reaction tubes. It was found that bromoform and carbon disulfide behave as ideal liquids with respect to additivity of volumes within experimental error incurred in using ordinary volumetric glassware.

The molar amount of carbon disulfide added to each reaction tube was selected to be in slight excess over that of the imine. The resulting reaction rate allowed significant imine disappearance with respect to time.

Infrared Method for Determination of Bis-(p-methoxy-phenyl)methyleneimine

A typical infrared spectrum of 0.2823 g of the imine dissolved in a solvent mixture of 0.8500 ml CHBr_3 brought to a total volume of 25.0 ml with CS_2 is shown in Figure 4. The baseline in this figure was obtained from the solvent mixture. Double beam operation with the solvent

mixture in the reference cell was used in all analyses. Typical instrument settings are shown in Table II.

TABLE II
Typical Instrument Settings for
Beckman IR-7 Analyses

Speed setting:	80, about $200\text{ cm}^{-1}/\text{min}$
Gain:	course 10, fine 5.08
Period:	2; slit schedule: 0.65 at 1000 cm^{-1}
Ordinate scale:	0-1 abs; DB
Linear wavenumber:	900 cm^{-1} , SB/DB set
Path:	0.5 mm, matched cavity cells

A demonstration of Beer's law obedience by the imine is shown in Figure 5.

The baseline value was greatly dependent upon the choice of wavenumber at which the single beam - double beam ratio was set for the instrument (Beckman IR-7). For these data 900 cm^{-1} was selected. Therefore, the baseline was true at 887 cm^{-1} . The technique of subtracting baseline absorbance from total absorbance gave the best Beer's law behavior, while the technique of using a "scribed" baseline also gave very good Beer's law behavior. For the band at 1363 cm^{-1} the baseline subtraction from total absorbance gave a positive intercept extrapolated to zero concentration. Use of the absorbance above a "scribed" baseline gave fairly good Beer's law behavior. The best analytical procedure resulted from setting the single beam - double beam ratio very near the wavelength to be studied.

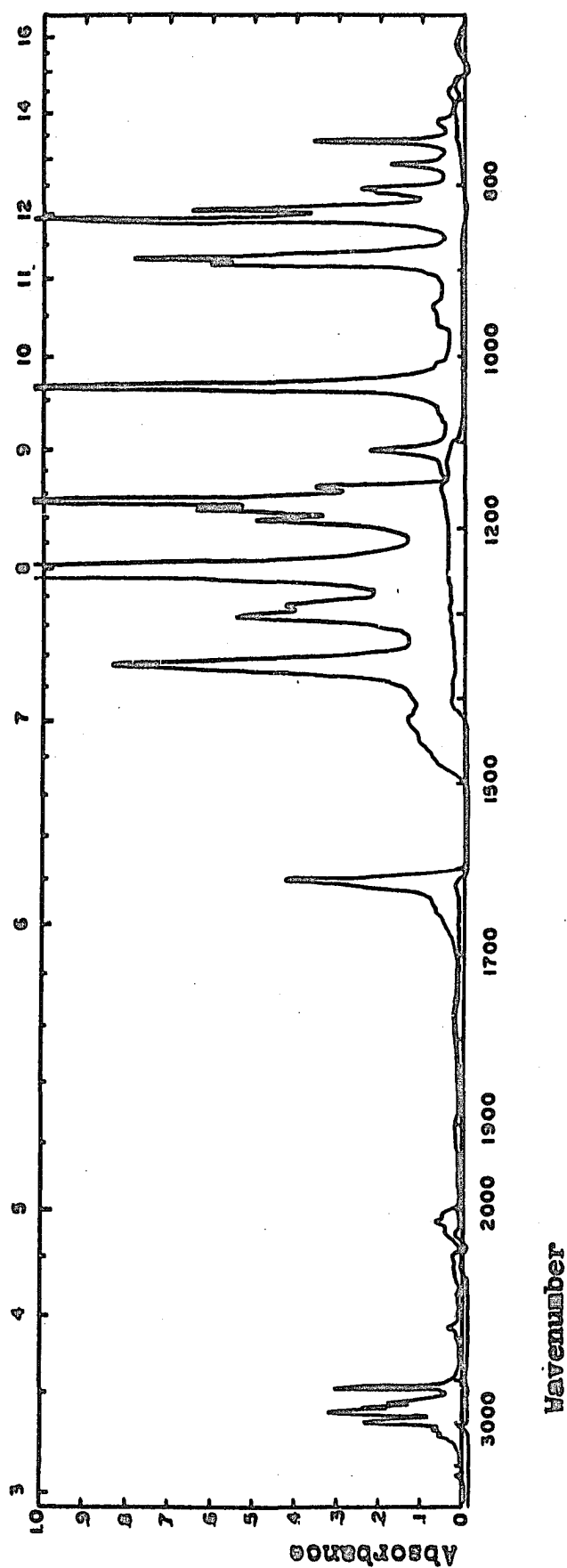


Figure 4. Analytical Infrared Spectrum of 0.2823 g Bis-(p-methoxyphenyl)-methylethimine Dissolved in 0.8500 ml CHBr_3 and Brought to 25.0 ml with CS_2 over a Baseline of the Solvent Mixture

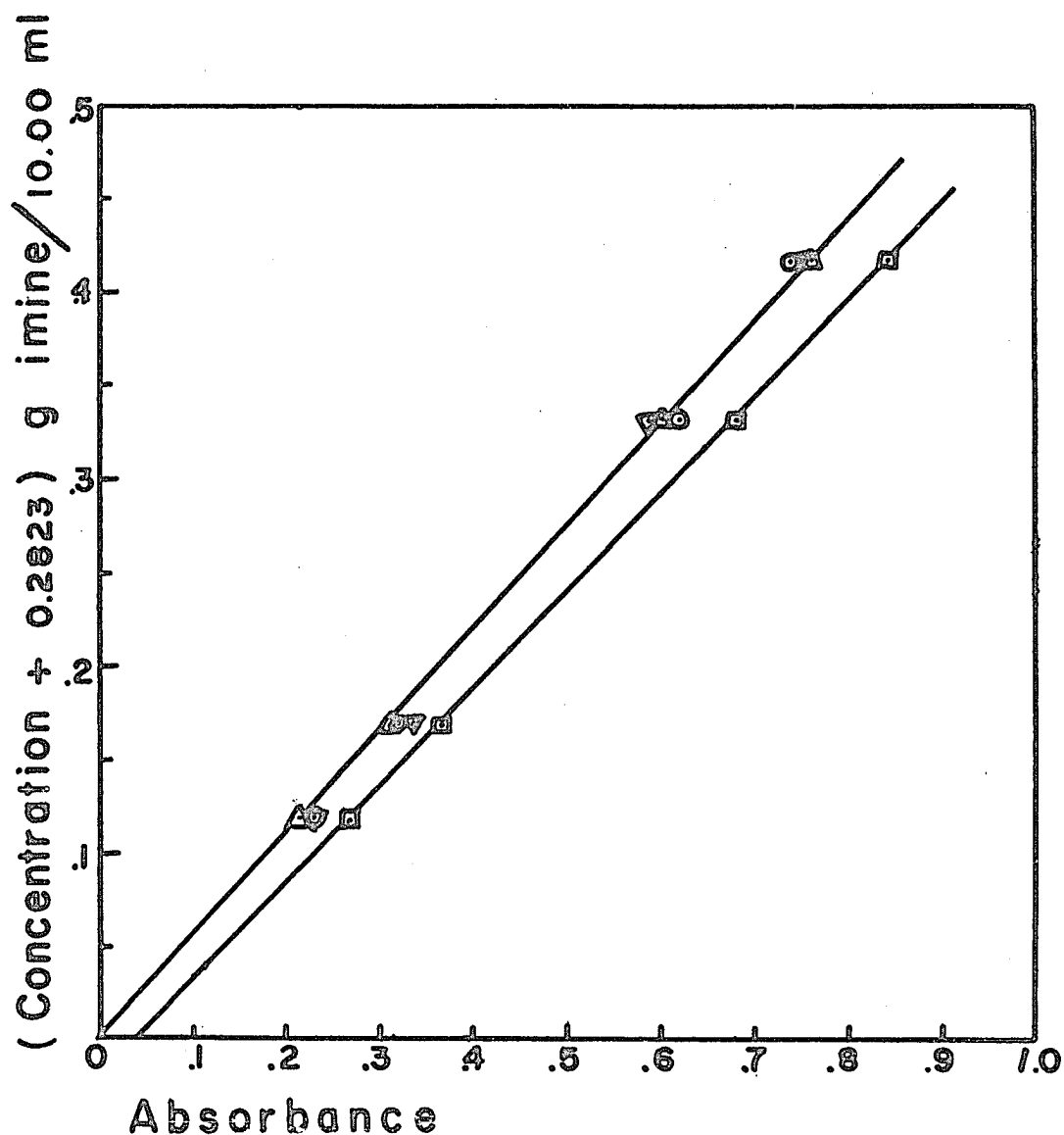


Figure 5. Demonstration of Beer's Law Obedience by Solutions of Bis-(p-methoxyphenyl)methyleneimine in a solvent mix of CS_2 and CHBr_3

- ▲ Absorbance above solvent mix baseline at 887 cm^{-1}
- Absorbance above solvent mix baseline at 1363 cm^{-1}
- Absorbance above scribed baseline at 887 cm^{-1}
- ▼ Absorbance above scribed baseline at 1363 cm^{-1}

(The scribed baseline was drawn between absorbance minima adjacent to the wavenumber of interest.)

Reproduction of instrumental behavior by always using the same settings was not expected. After Beer's law behavior was established in the concentration range to be studied, it was decided that one reaction tube of each kinetics run should be set aside as a standard. This tube was prepared in the same manner as the others but not heated. It was broken and its contents diluted to 25.0 ml with CS₂. The absorbance of the standard solution was measured and used to determine the moles of imine remaining in each of the other reaction tubes:

$$\text{Abs}_{2,3,\dots,12} \times \frac{\text{wt imine in tube 1}}{242 \times \text{Abs}_1} = \text{moles imine}_{2,3,\dots,12} .$$

The absorption band of the imine selected for infrared analyses was 887 cm⁻¹ (13). Examination of KBr disk spectra of other components present in the system showed negligible absorbance at 887 cm⁻¹.

Visible Method for Determination of 4,4'-Dimethoxythiobenzophenone

A typical visible-ultraviolet spectrum of the thioketone is shown in Figure 6.

The absorbance near 590 mμ was selected for analytical purposes instead of the stronger absorbance at 340 mμ, because CS₂ absorbs heavily near the latter wavelength. Determination of the extinction coefficient of 4,4'-dimethoxythiobenzophenone was done for several solvents. For CS₂ the extinction coefficient is shown in Figure 7. Table III

contains extinction coefficients for this compound in different solvents. Those determined in these laboratories were obtained from linear data similar to that in Figure 7.

The slope of the line in Figure 7 was found to be 2.662×10^{-3} moles l^{-1} cm abs^{-1} . Therefore, the molarity of thioketone in an analysis was:

$$abs \times 2.662 \times 10^{-3}.$$

When possible, each solution was suitably diluted to place the thioketone concentration in the concentration range which experimentally demonstrated Beer's law obedience.

TABLE III

λ_{max} (Visible) and Molar Extinction Coefficients
of 4,4'-Dimethoxythiobenzophenone
in Several Solvents (12)

Solvent	E(abs mole ⁻¹ l cm ⁻¹)	λ_{max}
Carbon disulfide	375*	593
Cyclohexane	317	590
n-Propanol	344	577
n-Propanol	314	568
Ethanol	277	570
Ethanol	278	577

*This corrects E in carbon disulfide cited in (12) as 266 to 375. The error was one of inversion.

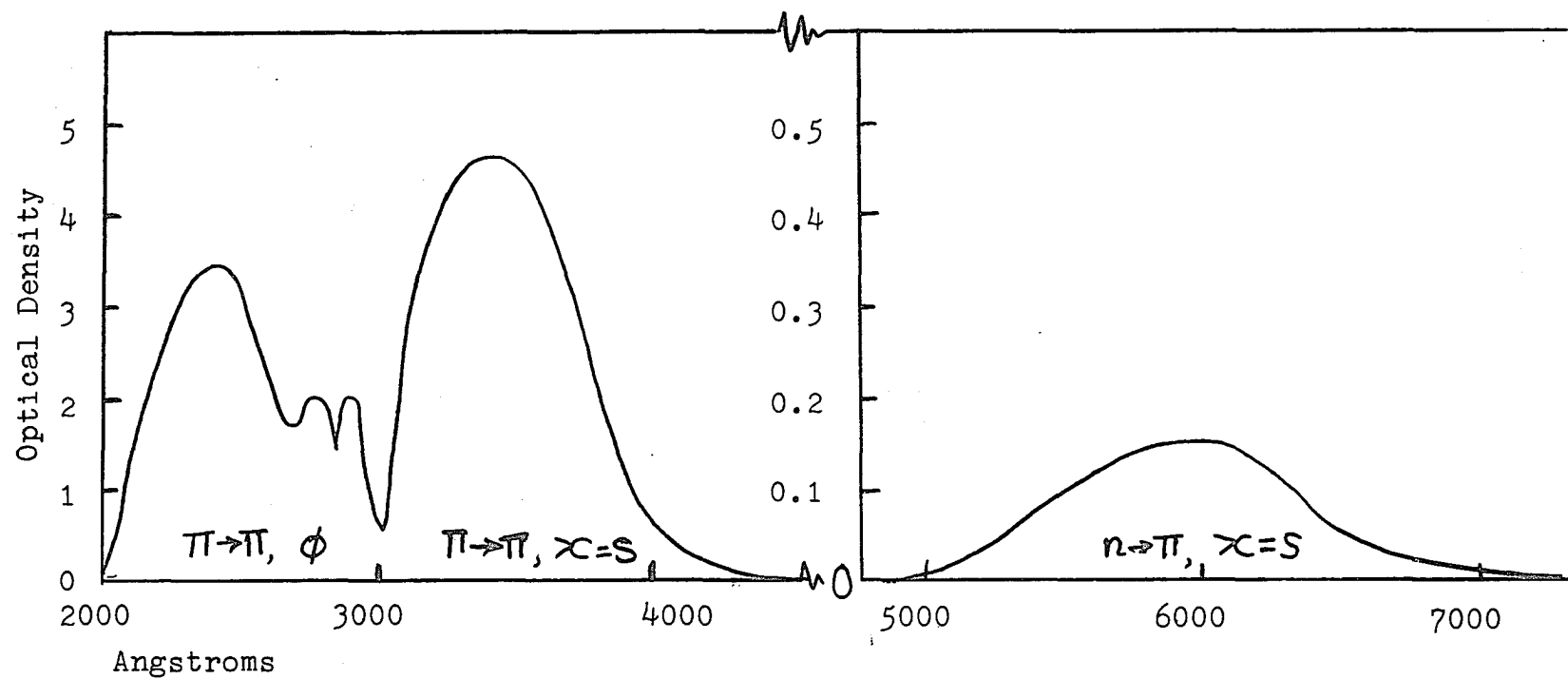


Figure 6. Ultraviolet-Visible Spectrum of 4,4'-Dimethoxythiobenzophenone in Cyclohexane (Obtained using a Cary Spectrophotometer, Model 15) The above assignments were made by the author.

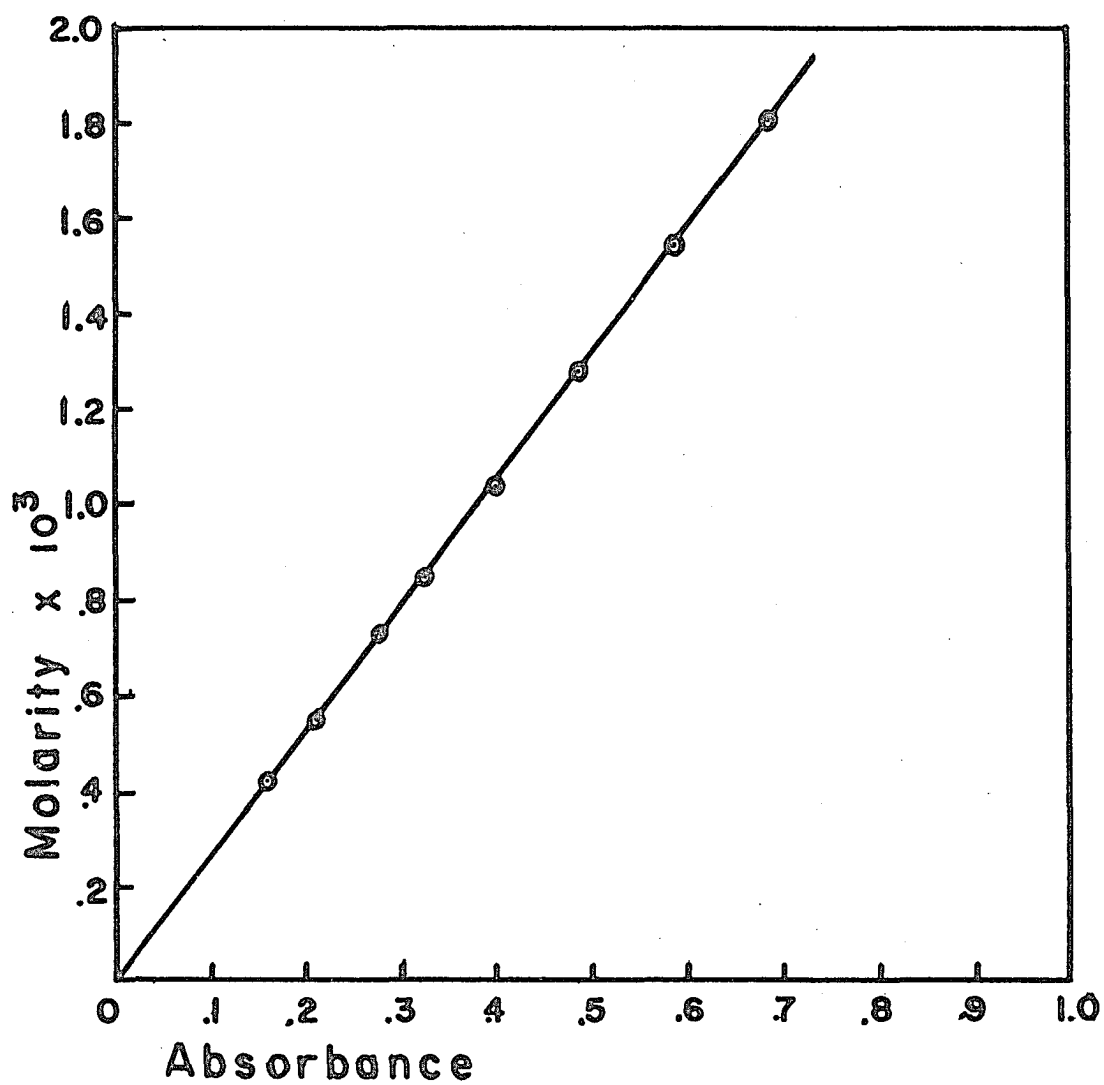


Figure 7. Extinction Coefficient Determination for 4,4'-Dimethoxythiobenzophenone in CS_2 .

Visible Method for Determination of CNS^-

Most of the iminium thiocyanate salt formed in reaction mixtures was recovered upon dilution of the tube contents with CS_2 . The salt crystallized upon slight cooling of the solution, but a small amount remained in solution. Attempts to recover measured amounts of the pure salt by diluting a bromoform solution of the salt with CS_2 resulted in about 95% recovery. The remainder of the salt was successfully determined as CNS^- by the method below. Summation of the weighed portions and those determined as CNS^- resulted in very good total analyses of the salt in several test cases.

The salt remaining in solution was extracted and determined according to the method discussed on pages 7 and 8. The standard curve shown in Figure 8 was obtained by treating standard potassium thiocyanate solution with the Fe (III) reagent.

From the standard curve it was determined that molarity of CNS^- in the final solution tested in the Beckman DB was:

$$(2.00 - \log \% T) \times 2.424 \times 10^{-4}, \text{ or} \\ \text{abs} \times 2.424 \times 10^{-4}.$$

When possible, each solution was suitably diluted to place the CNS^- concentration in the range which experimentally demonstrated Beer's law obedience.

Calibrations of nuclear magnetic resonance spectra are discussed along with results in Chapter V.

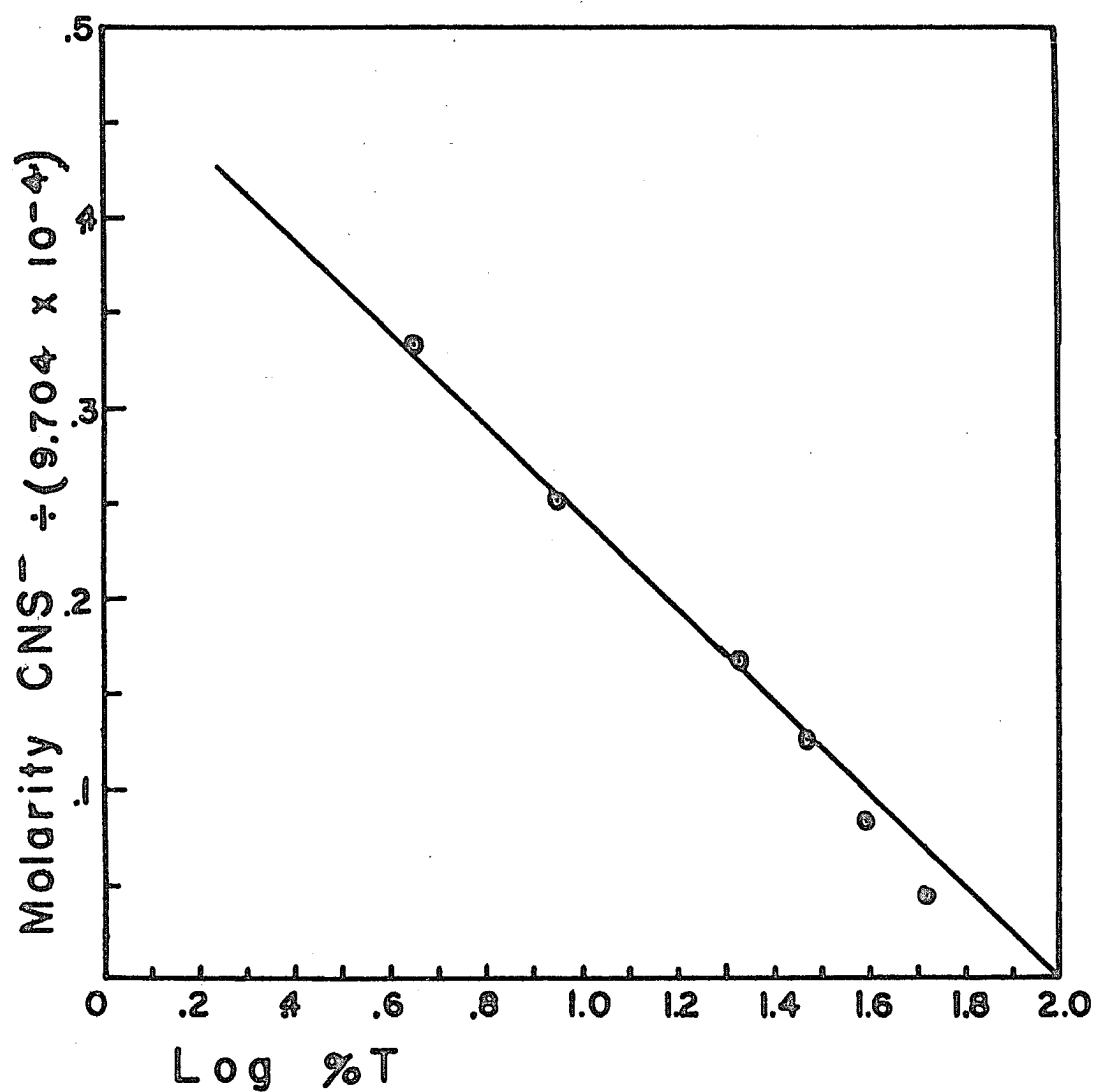


Figure 8. Determination of the Extinction Coefficient of Standard KCNS Solutions Treated with Excess Fe (III)

CHAPTER V

QUALITATIVE AND QUANTITATIVE RESULTS

Early studies of the reaction were carried out using nearly saturated solutions of bis-(p-methoxyphenyl)-methylenimine in CS_2 . Hilburn studied the rate of formation of 4,4'-dimethoxythiobenzophenone in these systems at 40°C by observing absorbance at 593 $\text{m}\mu$ in a quartz cell. Loudon studied the rate of disappearance of the imine in these systems at 40°C by observing absorbance at 887 cm^{-1} and 1363 cm^{-1} in a regular NaCl infrared cell. The rate of formation of crystals of the iminium thiocyanate was studied by direct weighing of the salt formed.

Curve "b" of Figure 9 illustrates the rate of disappearance of imine found by Loudon. He dissolved 0.1335 g imine in 10.00 ml CS_2 , and filled a regular infrared cell of 0.5 mm path length with a portion of this solution. The infrared beam heated the cell to 40°C ($\pm 1^\circ\text{C}$) within 15 minutes, and the temperature remained at this value throughout the experiment. This heating rate and the constancy of temperature were monitored by Loudon, who placed a thermometer in the immediate vicinity of the cell in the cell compartment of the Beckman IR-7.

Curve "a" of Figure 9 illustrates the growth and disappearance of a band at 2013 cm^{-1} observed by Loudon in the above experiment in which the reacting solution was in

contact with the copper metal cell spacer in the infrared cell used. This effect was not observed in the experiments done in the absence of copper.

Figure 10 illustrates the rate of disappearance of imine determined as follows. A solution was prepared by dissolving 0.2831 g imine in 25.00 ml CS_2 . The solution was divided into 20 glass tubes which were sealed with a torch. The tubes were placed in a 50.0°C ($\pm 0.1^\circ\text{C}$) water bath and separately taken out again at measured times, quenched in ice and stored in a refrigerator pending analysis. The contents of each tube were analyzed by the infrared method (matched cavity cells) discussed in the preceding chapter.

Results of the studies of Hilburn and Loudon seemed interesting and worthy of further study because the rate of disappearance of the imine was about ten times greater than the rate of appearance of known products. The reaction was then studied in sealed glass reaction vials at 40°C and the concentrations of imine, salt, and thioketone were determined for each vial. Within experimental error, a materials balance was obtained, i.e., at any time "t" the amount of imine which had disappeared could be approximately accounted for by the amounts of products formed. As the solution was placed in the infrared cell for imine analysis, the immediate formation of a yellow color in the solution was observed. This suggested that some component of the infrared cell was responsible for the anomalous rate in the early studies.

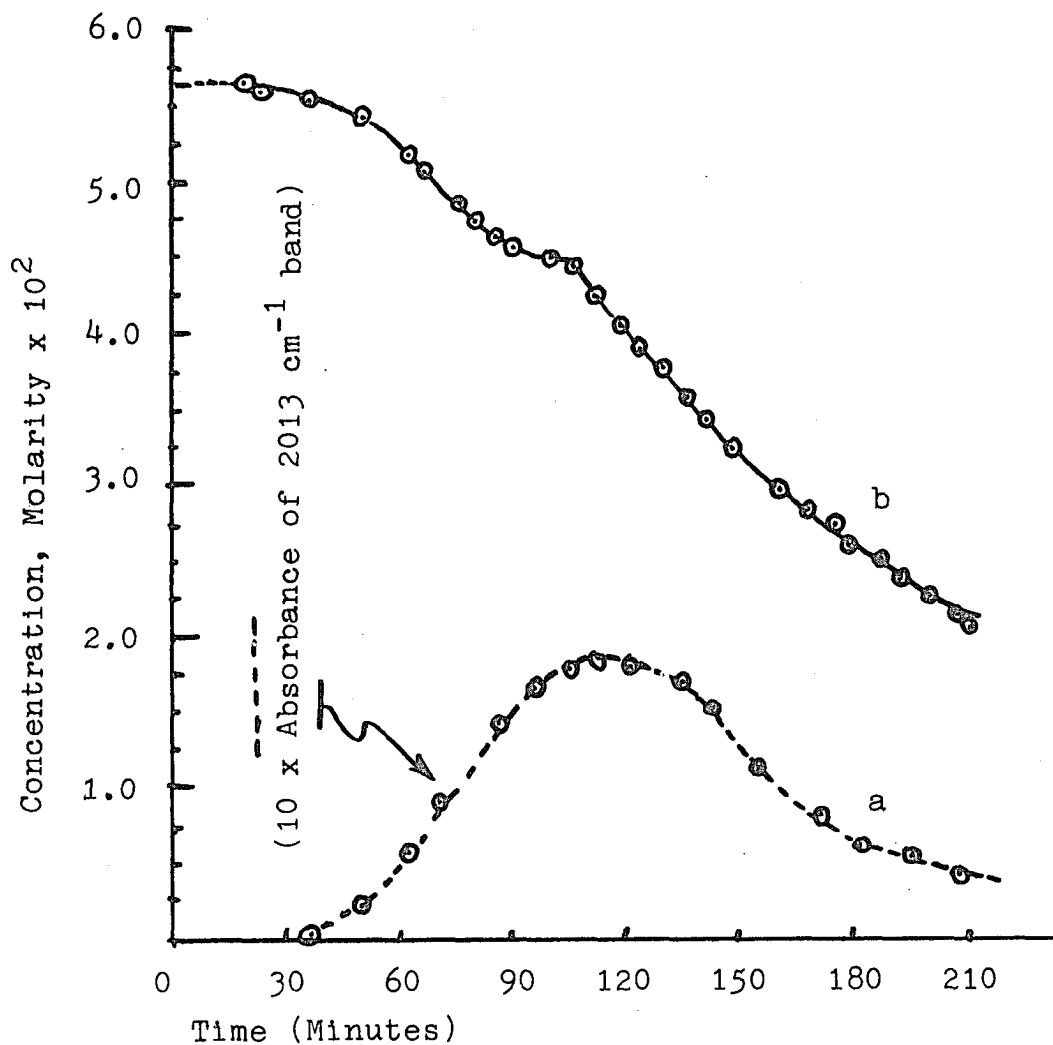


Figure 9. Imine Disappearance in CS_2 Solution in the Presence of Copper Metal at 40°C ($\pm 1^\circ\text{C}$)

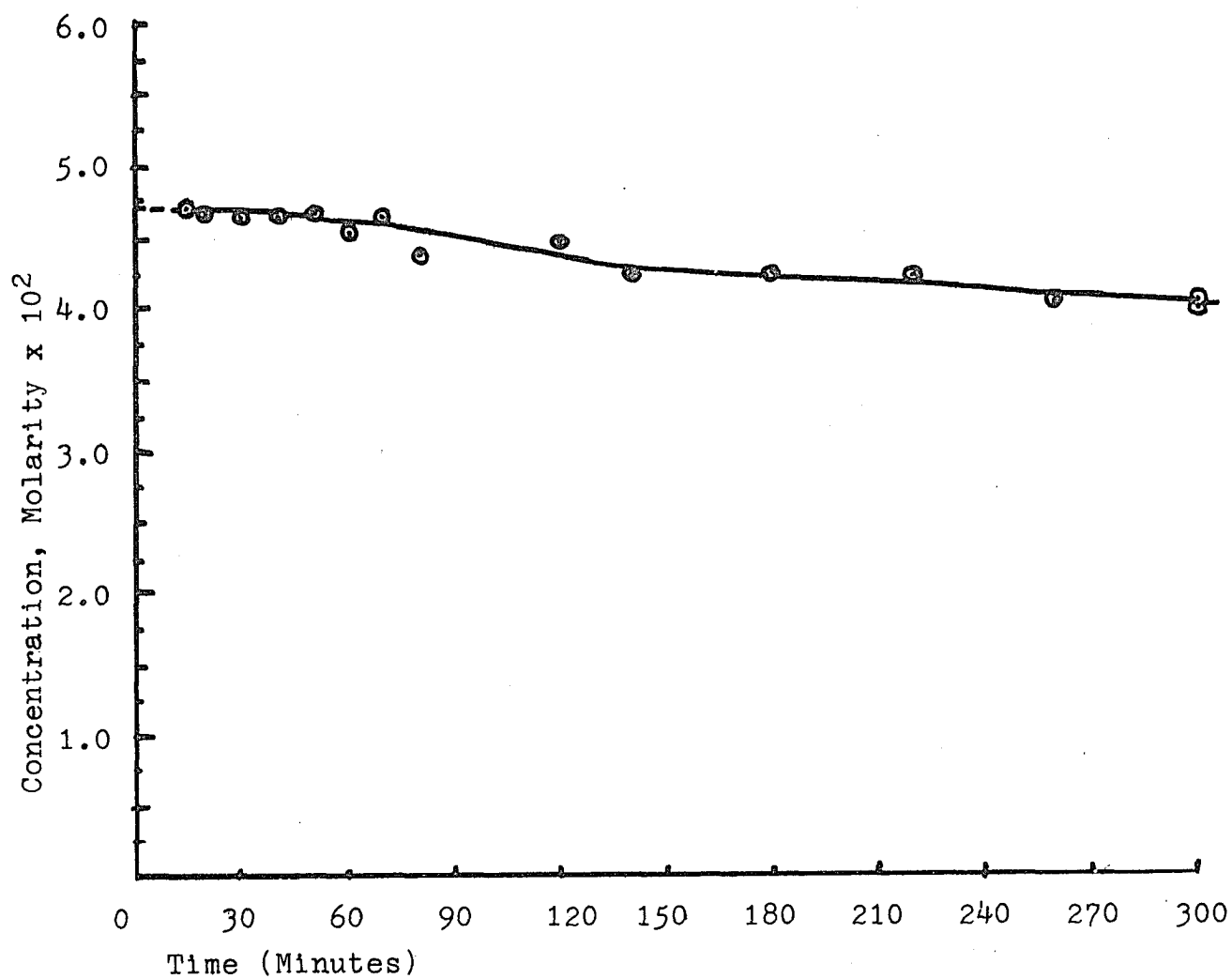


Figure 10. Imine Disappearance in CS_2 Solution in the Absence of Copper Metal at 50.0°C ($\pm 0.1^\circ\text{C}$)

The infrared cell was dismantled, and the effect of each component on rate of disappearance of imine was studied in glass containers. The only component affecting the rate was found to be the copper metal cell spacer. Although the rate of disappearance of imine was much more rapid in the presence of copper, the early rates of formation of salt and thioketone were nearly the same in the presence of copper metal as in its absence. This indicated that copper was not serving as a catalyst, but was probably a reactant.

Separate tests for the reactivity of polished copper foil and copper turnings toward imine dissolved in benzene, carbon tetrachloride, and cyclohexane were performed for periods of 48 hours at room temperature and at 40°C. The filtered liquid was evaporated to dryness, the residue treated with HNO_3 , evaporated to dryness, dissolved in a drop of water, and treated with NH_4OH . The formation of blue $\text{Cu}(\text{NH}_3)_4^{++}$ was not observed. Similar tests for copper and CS_2 indicated that CS_2 did not attack the copper foil.

The addition of a few drops of CS_2 to a solution of imine in benzene in the presence of polished copper foil resulted in the formation of a yellow color within minutes. An immediate test for copper in the liquid phase by the method above was negative, but a repetition of the test after about three hours was positive. The copper was visibly dissolved after 48 hours and the test for copper in the

liquid phase was indicative of copious amounts of copper. The blue color of thioketone in the solution was slight, indicating that imine + CS_2 reacted with the copper to divert the reaction from forming thioketone. A similar lack of the very slightly soluble iminium thiocyanate crystals likewise indicated diversion of the reaction. A benzene solution of thioketone stored over copper foil in the dark retained its blue color for a test period of about 24 hours, indicating no reaction between copper and the thioketone.

These observations indicated that the imine, CS_2 mixture was a rather powerful oxidizing agent, and that some substance existed in the liquid phase which could keep copper in solution. The substance was proposed to be N-[bis-(p-methoxyphenyl)methylene]dithiocarbamic acid, $(\text{CH}_3\text{OC}_6\text{H}_4)_2\text{C}=\text{NCSSH}$, by analogy with N,N-diethyldithiocarbamic acid, which is known to be a sensitive reagent for chelating Cu (II).

Efforts were made to trap N-[bis-(p-methoxyphenyl)-methylene]dithiocarbamic acid from the reaction mixture of imine and CS_2 . The reaction was carried out in absolute ethanol and sodium ethoxide was added in attempts to precipitate the sodium salt of the acid. Yields were very low and the precipitated material was in the form of extremely fine grains making recovery by filtration difficult. The grains were trapped in a glass filter frit, washed with absolute ethanol and dissolved in water. A trace of Cu (II) as aqueous CuSO_4 was added and a voluminous yellow precipitate immediately formed. Elemental analysis of the precipitate failed

to establish its formula as a Cu (II) chelate of the dithiocarbamic acid. The precipitate was only partly soluble in CS_2 . Most of a sample (61.3% by weight) of the yellow precipitate sublimed under 0.13 mm Hg at 130°C and was entrained and lost leaving a black residue, 38.7% by weight. The residue was examined by powder X-ray diffraction, and the diffraction pattern perfectly matched that of α -chalcocite, Cu_2S . The weight of Cu in the residue was only 0.306 of the Cu in the original sample of yellow precipitate. A substantial amount of the copper was carried away in the sublimation. Conclusions were that the precipitate was a mixture of substances and suffered oxidation-reduction changes on heating.

Many other attempts were made to prepare a stoichiometric compound from the reaction mixture of imine + CS_2 and selected metal ions. The imine was dissolved in ethanol and an aqueous solution containing the metal cation was added. An amount of CS_2 was added, calculated to be about twice the molar amount of imine in the system, and the system was held at 40°C for about four hours. Metals which gave precipitates were:

Hg (II) - a yellow precipitate

Pt (IV) - a dark brown precipitate

Cu (II) - a yellow precipitate.

Differential thermal analyses and thermogravimetric analyses indicated the above precipitates all had about the same decomposition pattern, decomposing between 140 - 180°C .

Infrared spectra (KBr disks) of the precipitates showed great similarities with a relatively large number of peaks, indicating some organic structure.

Further work is suggested for future studies in separation of these precipitates into pure components for elemental analyses. The kinetic data cited later in this chapter should be of value in improving yields.

While the above work was inconclusive, it indicated some credibility in the proposal of an addition product of imine and CS_2 to account for the solubility of copper in the system. On the basis of the known behavior of N,N-dimethyldithiocarbamic acid toward Cu (II) and of the formation of dithiocarbamates from CS_2 and various primary or secondary amines cited by Cotton and Wilkinson (1), it seemed reasonable to propose N-[bis-(p-methoxyphenyl)methylene] dithiocarbamic acid as the addition product.

Quantitative concentration versus time data are presented in Figures 11, 12, and 13, at 40°C , 50°C , and 60°C , respectively. One reaction vial allowed the determination of one point on each of the curves, "a", "b", and "c" of a given figure. The contents of each vial were prepared by dissolving an exact amount between 0.2817 and 0.2830 g imine in 0.8500 ml CHBr_3 and adding 0.1500 ml CS_2 , carefully preserving an interface between the liquids. The total volume of a vial containing 0.2829 g imine, 0.8500 ml CHBr_3 , and 0.1500 ml CS_2 was determined to be 1.26 ml (± 0.01 ml). Each vial was brought to the desired reaction

temperature and rapidly shaken, left at the reaction temperature for a given time, "t", and quenched in ice-brine solution. The analytical results for each vial were normalized to an initial imine weight equal to that in the vial selected as a standard (blank) for that kinetics run. Total volume in all vials was the same and did not appear to change in the course of the reaction. In Figures 11, 12, and 13, curve "a" represents moles of thioketone formed as determined by absorbance at 593 m μ , and moles of iminium thiocyanate formed as determined by summation of weighed salt crystals and salt determined colorimetrically at 461 m μ as the extracted CNS⁻. Within experimental error, moles of salt and thioketone were the same at all times. Curve "b" represents moles of imine remaining as determined by absorbance at 887 cm⁻¹. Curve "c" was constructed from curves "a" and "b" and represents (2 x "a") + "b".

The points on curve "c" which lie on a horizontal line intersecting the number of moles axis at the initial imine concentration represent a good materials balance accounting for all disappeared imine in the formation of salt and thioketone. All three kinetics runs demonstrate a reasonable materials balance at later reaction times which indicated that errors in the analytical methods were reasonably small. The noticeable deviations from a materials balance early in runs at 50°C and 60°C were not due to analytical errors. The conclusion was that some substance involving the imine was temporarily formed but later was transformed completely to thioketone and salt.

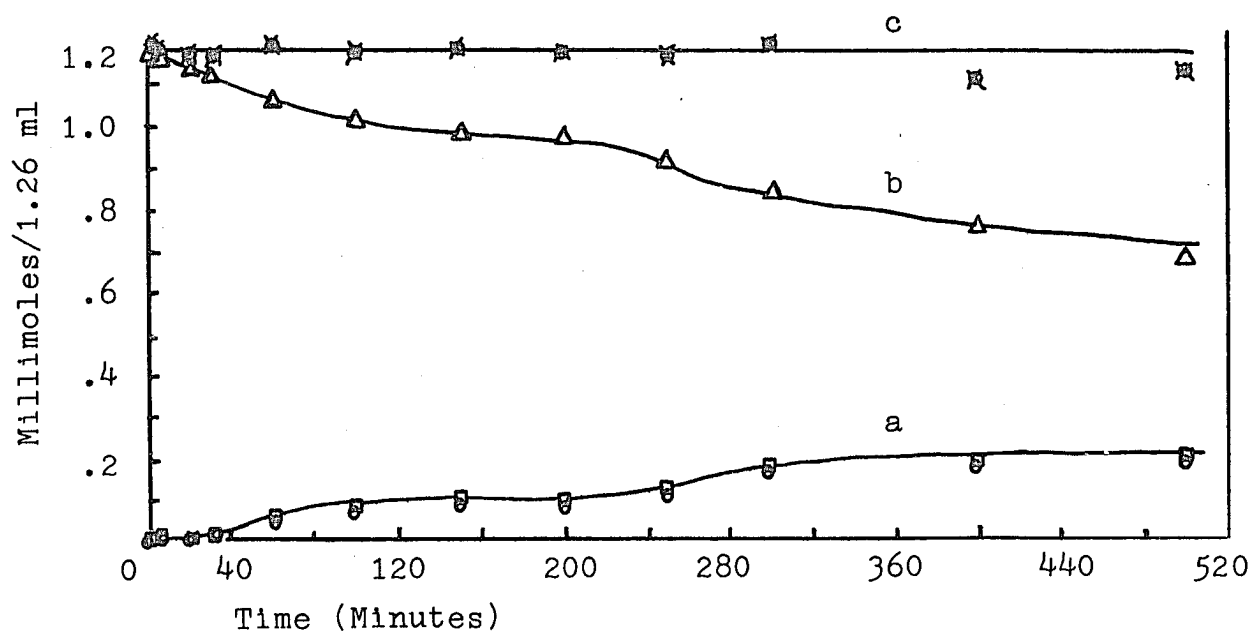


Figure 11. Analyses of Reaction Mixtures at 40°C

a ○ Iminium Thiocyanate

□ Thioketone

b △ Imine

c ■ Materials Balance: $(2 \times a) + b$

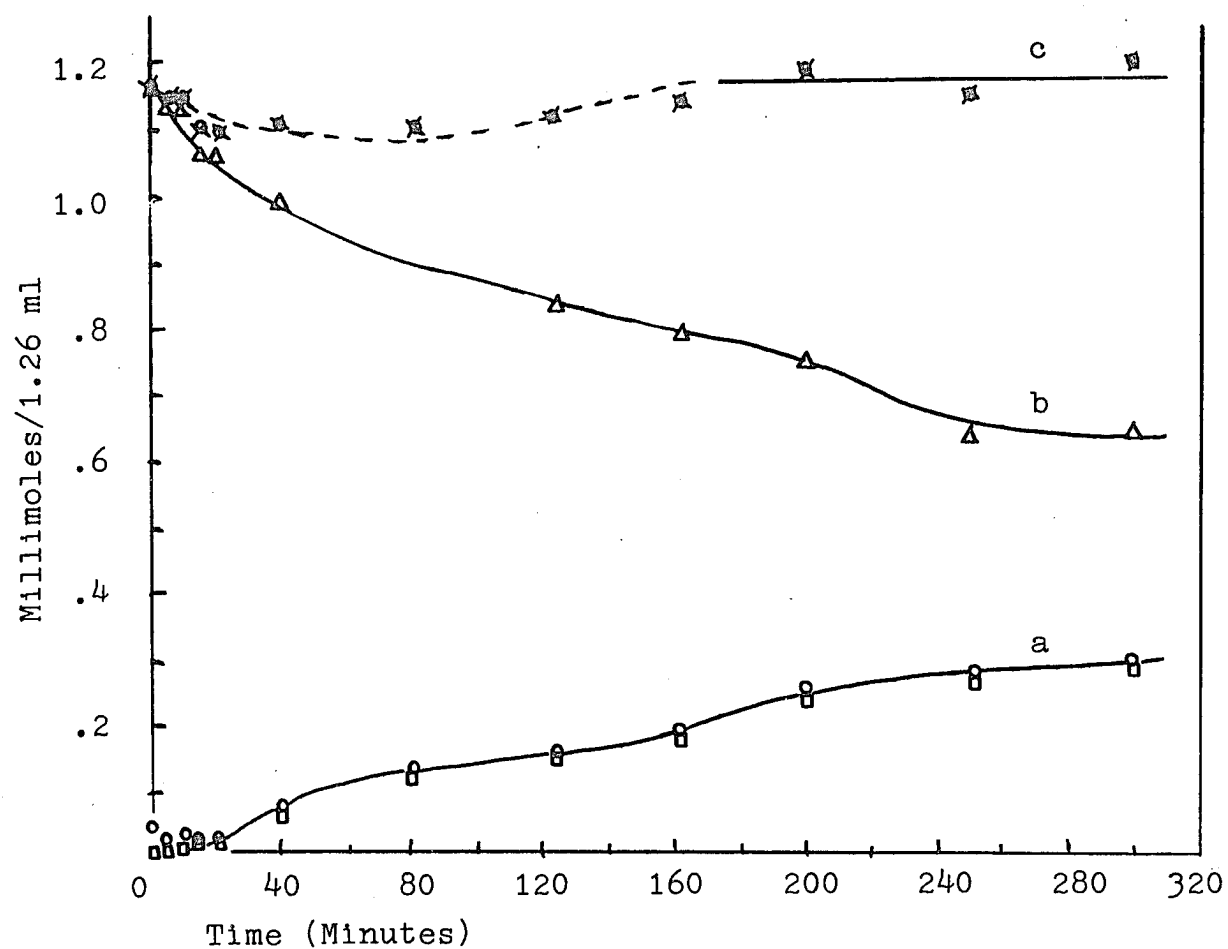


Figure 12. Analyses of Reaction Mixtures at 50°C

a ○ Iminium Thiocyanate

□ Thioketone

b △ Imine

c ▣ Materials Balance: $(2 \times a) + b$

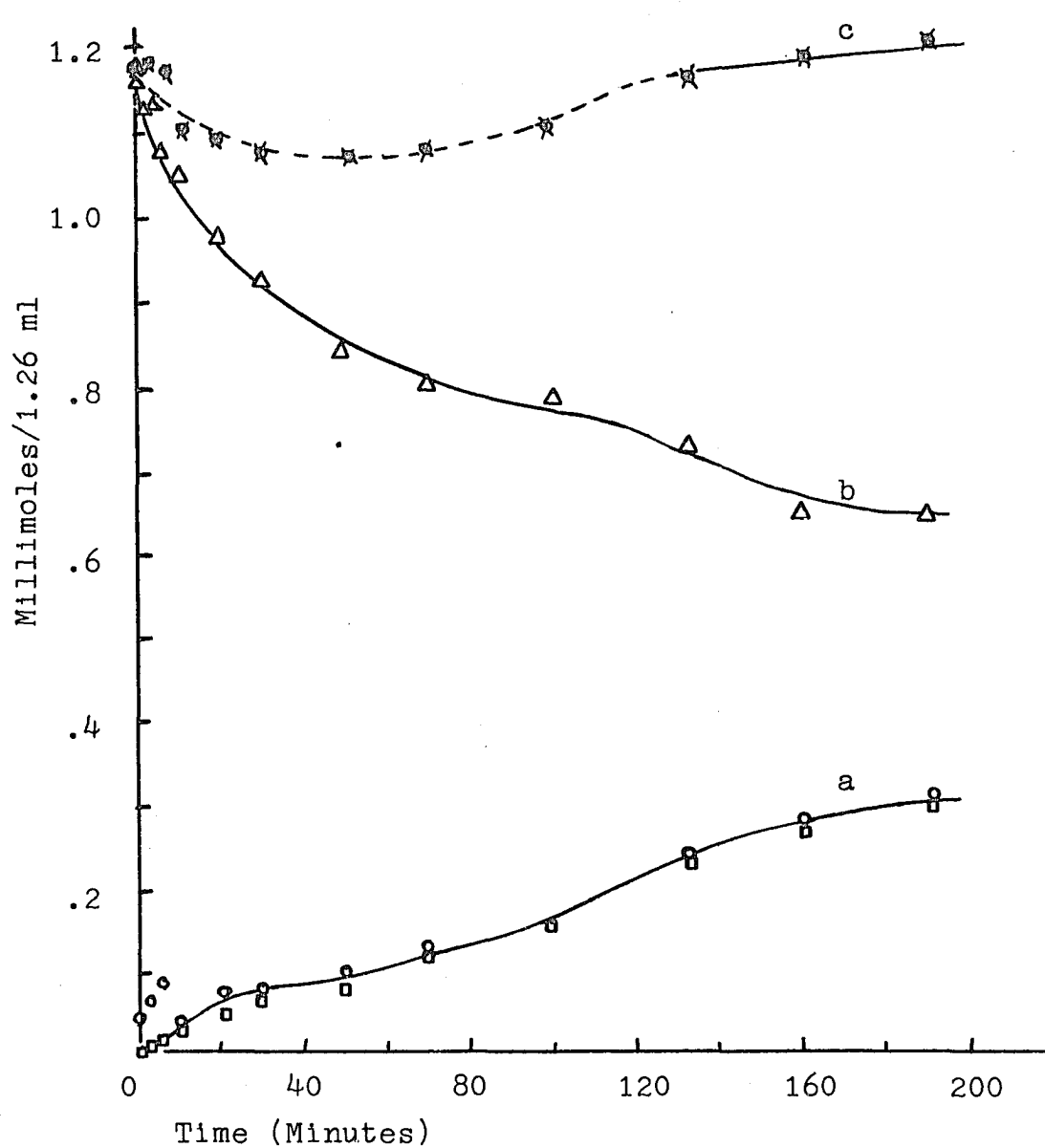
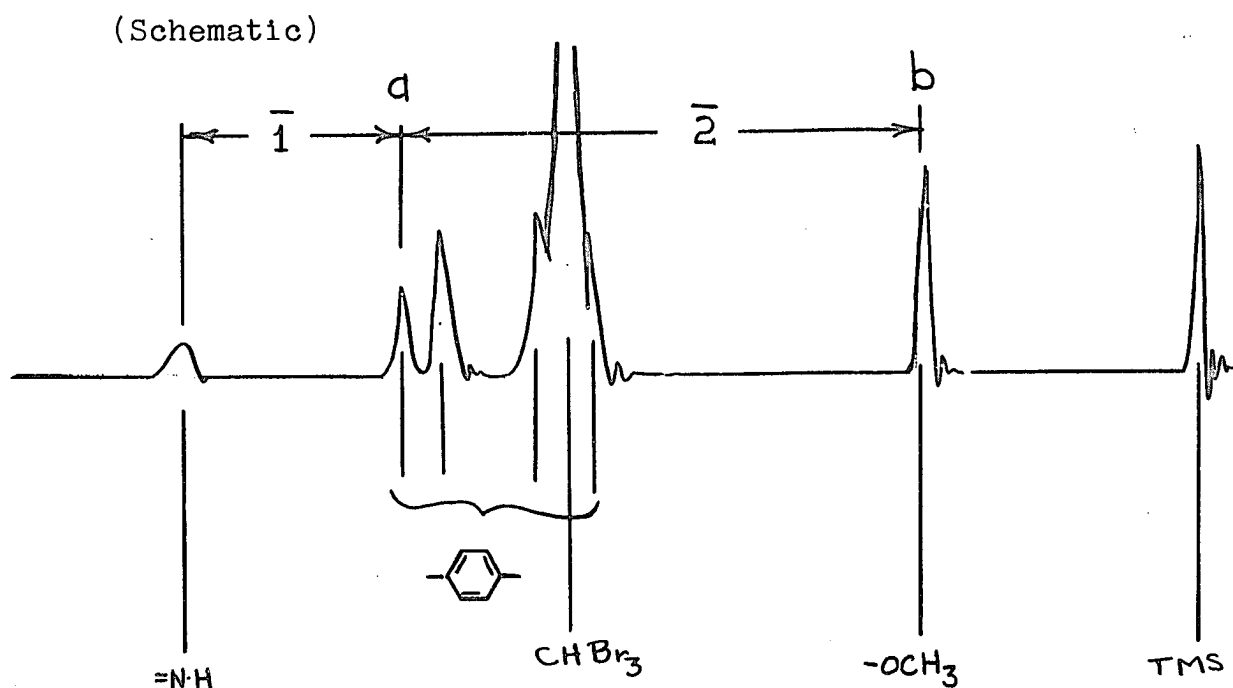


Figure 13. Analyses of Reaction Mixtures at 60°C

- a ○ Iminium Thiocyanate
- Thioketone
- b △ Imine
- c ✕ Materials Balance (2 x a) + b

Figure 14 shows time dependence of a nuclear magnetic resonance downfield shift in the N-proton peak of the imine during the course of the imine, CS_2 reaction at 40° , 50° , and 60° . Each curve was constructed from successive data points taken from NMR spectra run on one reaction tube prepared as described earlier. The initial NMR spectrum of the imine was as curve "a" of Figure 15. Peak assignments were:



Calibration of this spectrum was performed by Dr. W. L. Senn of Esso Research Labs, Baton Rouge, Louisiana, using a Varian Nuclear Magnetic Resonance Spectrometer, Model A-60, and internal standards. The kinetic data cited in Figure 14 were taken in these laboratories using a Varian NMR Spectrometer, Model HR-60, prior to installation of a

proton stabilizer attachment. During the kinetics runs the field was subject to shift. This effect was compensated by measuring both distances $\bar{1}$ and $\bar{2}$ above for each data point in Figure 14. Calibration placed peak "a" at 452 cps and peak "b" at 221 cps, with reference to tetramethylsilane at zero. Therefore, since $452 - 221 = 231$, it follows that:

$$\frac{\bar{1}}{\bar{2}} \times 231 \text{ cps} + 231 \text{ cps} + 221 \text{ cps} = \text{cps of peak "c", the moving peak.}$$

This method was subject to error in that reference point "a" shifted slightly downfield toward the end of a given kinetics run. Curve "b" of Figure 13 shows that in the limit of pure salt, distance $\bar{2}$ has increased by about 10%. This could cause an error of about 3% in the position of peak "c".

Figure 15 shows several NMR spectra taken in these laboratories after installation of the proton stabilizer attachment. Calibrations done here using this attachment and internal standards were within 5 cps of those done by Dr. W. Sen. Assignment of the peaks of these spectra are the same as those made on page 42, except for the most downfield peak in curves "b", "c", "d", and "e" and two of the peaks in curve "f". The solvent used in obtaining curve "f" was CHCl_3 which had a large peak at 440 cps. For clarity in the drawing of Figure 15 a few peaks' apexes were deleted above dotted lines.

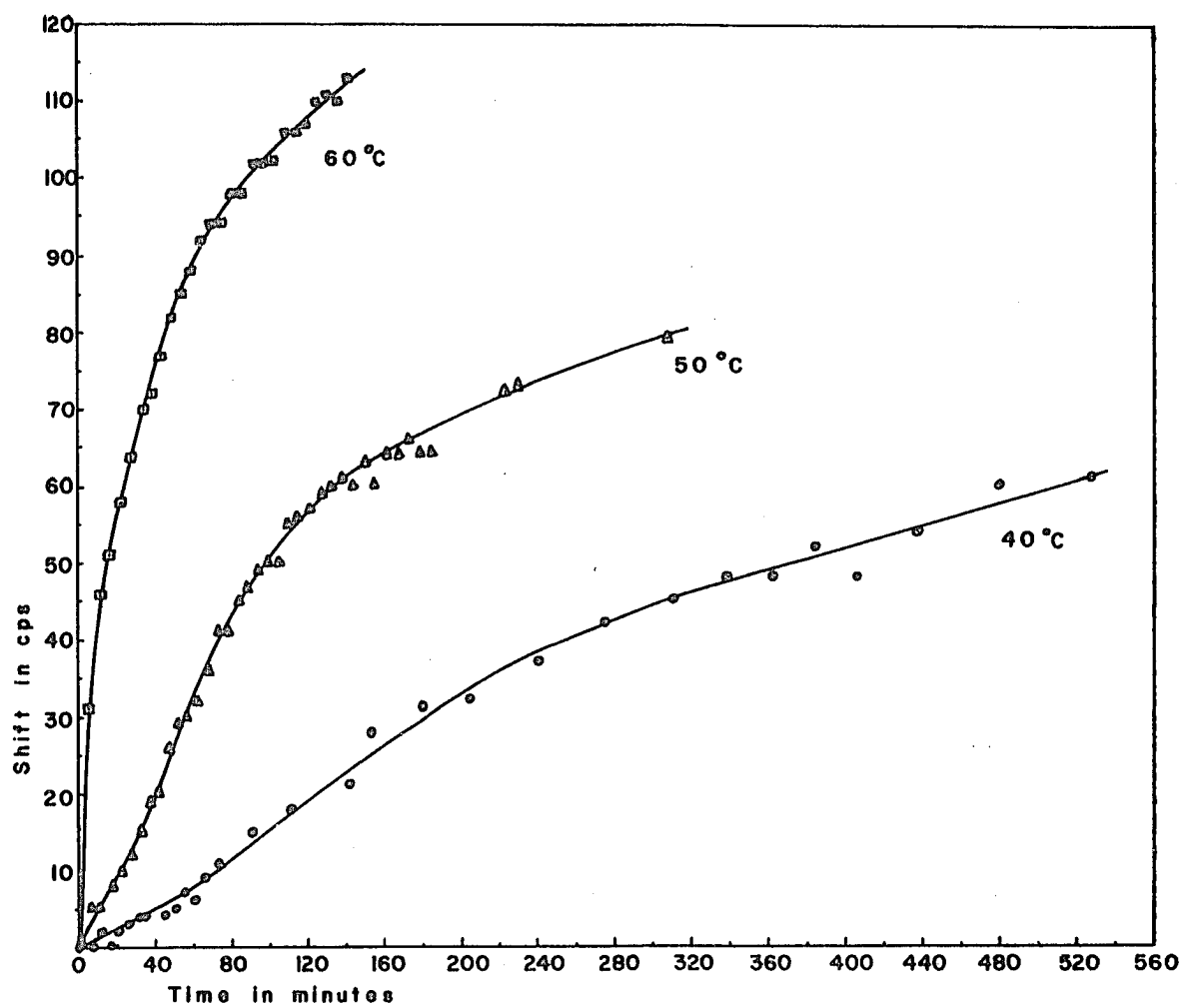


Figure 14. Downfield NMR shift of imine N-proton

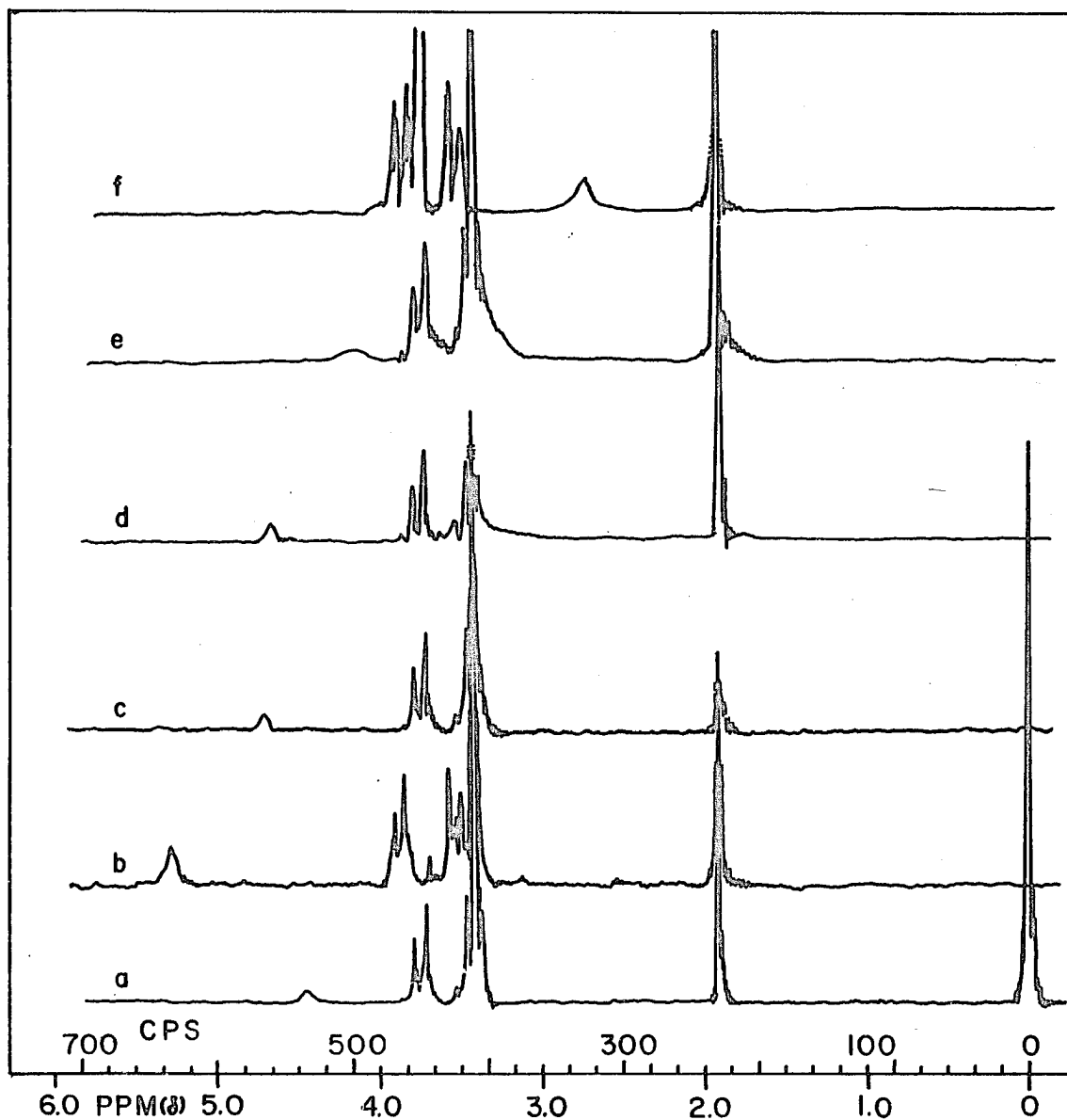


Figure 15. Nuclear Magnetic Resonance Spectra

- a. Bis-(p-methoxyphenyl)methyleneimine in CHBr_3
- b. Bis-(p-methoxyphenyl)methyleneiminium thiocyanate in CHBr_3
- c. Mixture of a and b or typical (imine + CS_2) mixture in reaction in CHBr_3
- d. HCl gas bubbled into the imine in CHBr_3 for about one minute
- e. CHBr_3 solution of the imine to which three drops of CHBr_3 treated to NH_3 for one minute are added
- f. H_2S gas bubbled into the imine in CHCl_3 for about five minutes

Curve "a" of Figure 15 is the NMR spectrum of 0.2823 g imine dissolved in 1.000 ml CHBr_3 . Curve "b" is the spectrum of a saturated solution of iminium thiocyanate in CHBr_3 . The downfield peak of curve "b" is assigned as $=\text{N} \begin{smallmatrix} \text{H} \\ \text{H} \end{smallmatrix} \oplus$. Curve "c" is a typical spectrum of a reaction mixture of imine + CS_2 in CHBr_3 . The downfield peak of curve "c" was considered to be some kind of complex average of molar quantities of the two species $=\text{N} \begin{smallmatrix} \text{H} \\ \text{H} \end{smallmatrix} \oplus$ and $=\text{N}-\text{H}$. Curve "c" is also typical of the spectrum of a mixture of imine and iminium thiocyanate. The absence of two peaks in this spectrum was the basis for assuming that a rapid proton exchange between $=\text{N} \begin{smallmatrix} \text{H} \\ \text{H} \end{smallmatrix} \oplus$ and $=\text{N}-\text{H}$ accounted for the single peak which was observed to move downfield in curve "c". Curve "d" is a spectrum of a solution of imine in CHBr_3 into which HCl gas or HBr has been passed for about one minute. Rapid protonation of the imine and proton exchange between the two species is suggested by the position of the single downfield peak. Curve "e" in the spectrum was obtained from one milliliter of an imine, CHBr_3 solution into which were added three drops of a solution made by passing NH_3 through CHBr_3 for one minute. The downfield peak moved upfield and lost resolution as the concentration of NH_3 was increased. This indicates a proton exchange between $=\text{N}-\text{H}$ and NH_3 with loss of resolution ascribed to increased quadrupole coupling between protons and N as the concentration of NH_3 increased. Curve "f" is the spectrum obtained by passing H_2S through a solution of

imine in CHCl_3 . The downfield peak moved upfield with time, and is seen in curve "f" to be between the di-substituted phenyl peaks and the methoxy peaks after about five minutes treatment with H_2S . This effect will be discussed more thoroughly in a later chapter.

The shift in the imine N-proton peak was studied with respect to iminium thiocyanate concentration. A solution of 0.2820 g imine plus 1.00 ml CHBr_3 was prepared, and a solution of 0.1761 g iminium thiocyanate plus 1.50 ml CHBr_3 was prepared. Total volumes of these solutions were 1.26 ml and 1.65 ml (± 0.01 ml), respectively. Table IV gives results of NMR spectra of mixtures of these solutions. The spectra were obtained at room temperature within three minutes of mixing and peak positions were found to be independent of temperature. System 2 gave the same NMR spectrum after five minute intervals of vigorous mixing. The spectrum of system 3 likewise did not change with time and vigorous mixing. System 4 gave the same spectrum after 25 minutes of heating at about 60°C .

Figure 16 was obtained by plotting the observed =N-H peak's downfield shift against the ratio of molarity of iminium thiocyanate, M_s , to molarity of imine, M_i , in the system.

TABLE IV
Calibration of =N-H NMR Peak Shift as
a Function of $=N\begin{smallmatrix} H \\ \diagdown \\ H \end{smallmatrix}CNS$

System Number	Volume of Imine Sol'n ml (\pm 0.01 ml)	Volume of Salt Sol'n ml (\pm 0.01 ml)	Total Volume ml (\pm 0.01 ml)	Observed Downfield Shift from Imine =N-H Peak (cps)
1	1.03	0.00	1.03	0
2	1.03	0.18	1.21	18
3	1.03	0.48	1.51	24
4	1.03	0.86	1.89	32
5	1.03	1.34	2.37	48

The iminium thiocyanate was soluble enough in $CHBr_3$ that crystals did not appear in reaction vials during kinetics runs. However, addition of 20 ml of CS_2 to the vial contents caused crystals of salt to form. The dielectric constant of $CHBr_3$ is low, but the high solubility of the salt in $CHBr_3$ made it necessary to determine if the salt were dissociated in $CHBr_3$. The resistance of a saturated solution of iminium thiocyanate in $CHBr_3$ was measured and found to be greater than 2.5 megohms in a cell of cell constant approximately equal to 0.014 cm^{-1} . The conclusion was that the salt was either un-dissociated in $CHBr_3$ or existed as intimate ion pairs.

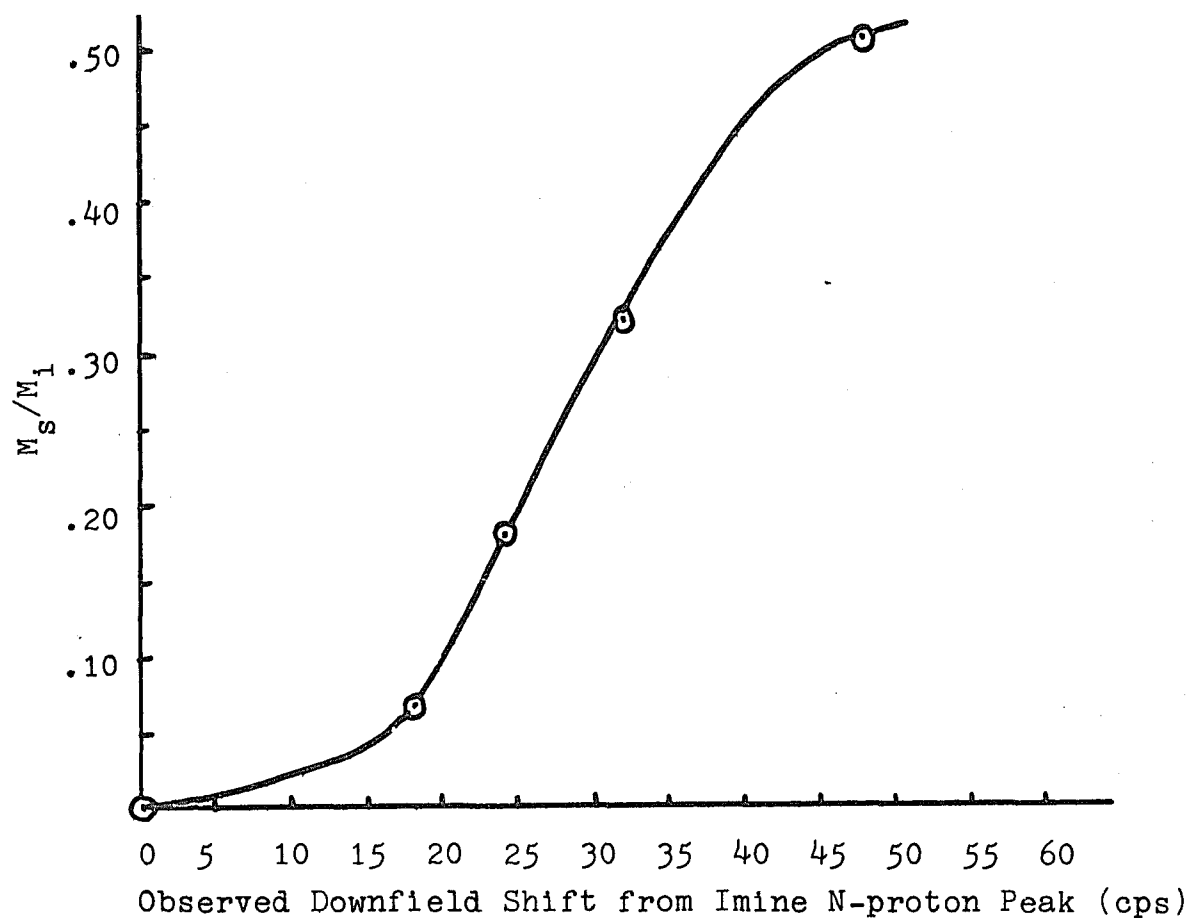


Figure 16. N-proton NMR Peak Position as a Function of the Ratio of Molarities of Iminium Thiocyanate to Imine

CHAPTER VI

CONCLUSIONS

The effect of relative iminium thiocyanate to imine concentrations on the position of the N-proton peak in the NMR spectrum has been shown in Figure 16. Concentrations of imine and iminium thiocyanate taken from the quantitative kinetics runs of Figures 11, 12, and 13, were used to construct Tables V, VI, and VII. The following terms of these tables were defined as:

M_s : molarity of iminium thiocyanate

M_i : molarity of imine

$\Delta_{\text{Fig 16}}$: the downfield shift of the imine N-H band as a function of iminium thiocyanate to imine concentrations

$\Delta_{\text{Fig 14}}$: the observed downfield shift of the imine N-H band in kinetics runs.

It is emphasized here that iminium thiocyanate was determined as precipitated crystals plus extracted CNS^- , and that a determination of $=\text{N}\begin{smallmatrix} \text{H} \\ \text{H} \end{smallmatrix}^{\oplus}$ in the system could not be made directly.

A mechanism requiring $=\text{N}\begin{smallmatrix} \text{H} \\ \text{H} \end{smallmatrix}^{\oplus}$ in the system in excess of $=\text{N}\begin{smallmatrix} \text{H} \\ \text{H} \end{smallmatrix}^{\oplus}$ determined as iminium thiocyanate might partially have explained the differences in the following tables. However, a quantitative treatment was not feasible, because the position of the $=\text{N}\begin{smallmatrix} \text{H} \\ \text{H} \end{smallmatrix}^{\oplus} \oplus \text{X}$ nitrogen proton peak was not known.

TABLE V
Salt Shift and Shift Observed at 40°C

Time (min)	$\frac{M_s}{M_1}$	$\Delta_{\text{Fig 16}}$ (salt) (cps)	$\Delta_{\text{Fig 14}}$ (observed) (cps)
40	0.003	1-2	5
80	0.064	16	11
120	0.087	19	19
160	0.088	19	25
200	0.101	21	33
240	0.130	22	38
280	0.181	24	42
320	0.223	27	46

TABLE VI
Salt Shift and Shift Observed at 50°C

Time (min)	$\frac{M_s}{M_1}$	$\Delta_{\text{Fig 16}}$ (salt) (cps)	$\Delta_{\text{Fig 14}}$ (observed) (cps)
40	0.070	17	21
80	0.137	23	43
120	0.172	23	57
160	0.226	27	64
200	0.322	32	70
240	0.406	37	74
280	0.447	40	77

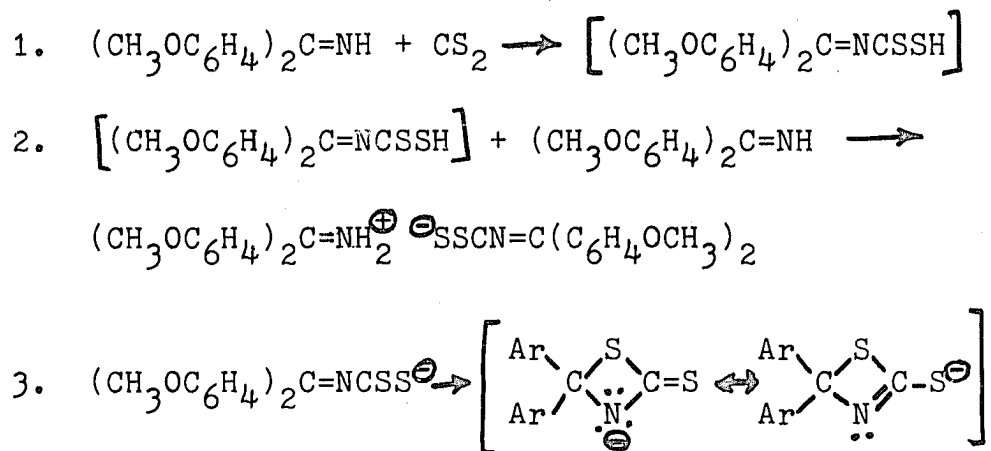
TABLE VII
Salt Shift and Shift Observed at 60°C

Time (min)	$\frac{M_s}{M_i}$	$\Delta_{\text{Fig 16}}^{(\text{salt})}$ (cps)	$\Delta_{\text{Fig 14}}^{(\text{observed})}$ (cps)
20	0.062	16	55
40	0.090	19	75
60	0.120	21	89
80	0.152	23	97
100	0.209	26	103
120	0.271	29	110

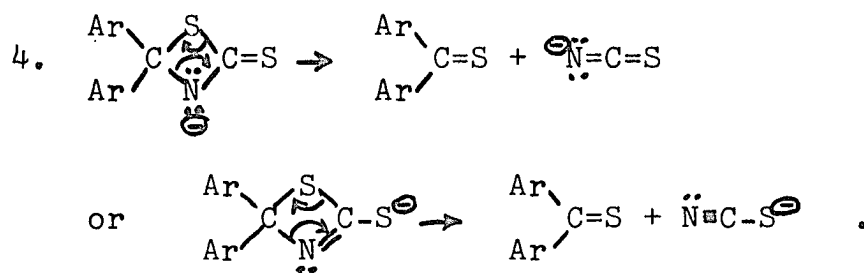
The mechanism of the reaction between carbon disulfide and bis-(p-methoxyphenyl)methyleneimine must account for the following:

1. Simultaneous formation of the thioketone and iminium thiocyanate in equal amounts (see Figures 11, 12, and 13)
2. Formation of some substance in the reaction mixture which would:
 - (a) be diverted by reaction with Cu (II) to cause a greater rate of imine disappearance than in the absence of Cu (II)
 - (b) account for imine disappearing but not appearing immediately as thioketone and iminium thiocyanate
 - (c) cause greater NMR shifts of the nitrogen proton peak than does iminium thiocyanate alone
 - (d) finally yield thioketone and iminium thiocyanate

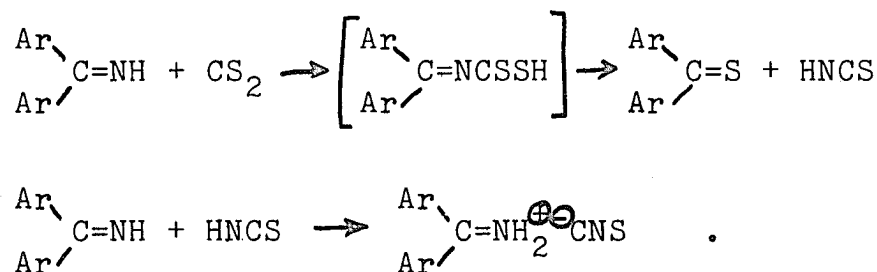
The following mechanism which accounts for the above requirements is proposed as mechanism I:



by nucleophylic attack and promoted by resonance stabilization



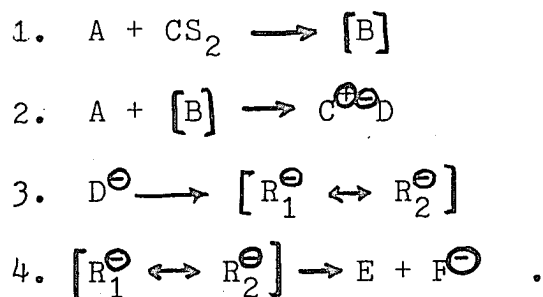
An alternative mechanism II could be:



Mechanism II accounted for formation of final products and the temporary departure from a materials balance. One possible weakness was in the requirement

that an intermediate acid substance could coexist with the imine while HNCS was required to react rapidly with the imine. This mechanism did not account for the rearrangement necessary in forming the thioketone. Also, it did not provide the anion of the dithiocarbamic acid, which should be more reactive toward Cu (II) than the undissociated dithiocarbamic acid.

Mechanism I may be rewritten for convenience as:

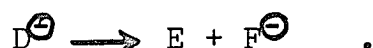


Figures 11, 12, and 13 show differential kinetic data as overall $\frac{dA}{dt}$ and $\frac{dE}{dt} = \frac{dF^{\ominus}}{dt}$ from curves "a" and "b", respectively. The mechanism proposed had steps (3) and (4) which involved internal rearrangements which were assumed to be independent of diffusion control. This accounted for a build-up of $C^{\oplus}D^{\ominus}$ early in the reaction at higher temperatures and may be correlated with the minima in curves "c" of Figures 12 and 13. The minima in curves "c" are thought to be due to equal rates of formation and disappearance of D^{\ominus} . The rate of formation is collision dependent and therefore diffusion controlled, and the rate of disappearance through internal rearrangement is not diffusion controlled. The

rate of formation of D^{\ominus} increases more with an increase in temperature than does the rate of disappearance of D^{\ominus} .

Step (2) was assumed to be rapid in accordance with observed rapid protonations of the imine with HCl and HBr and the large observed NMR shifts in Figure 15.

These assumptions, if valid, would reduce the number of rate controlling factors to two reaction sequences. Early in the reaction there would be two rate controlling factors:



Concentration of C^{\oplus} would equal those of $F^{\ominus} + D^{\ominus}$ and equal to the amount of imine not accounted for in the formation of thioketone, E, and iminium thiocyanate, $C^{\oplus}F^{\ominus}$. Later in the reaction the decay of D^{\ominus} might not be a rate controlling factor, and:



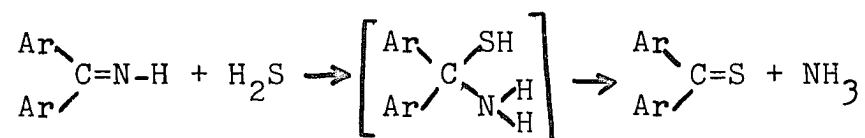
after the concentration of imine and CS_2 may have become too low to allow build-up of $C^{\oplus}D^{\ominus}$.

CHAPTER VII

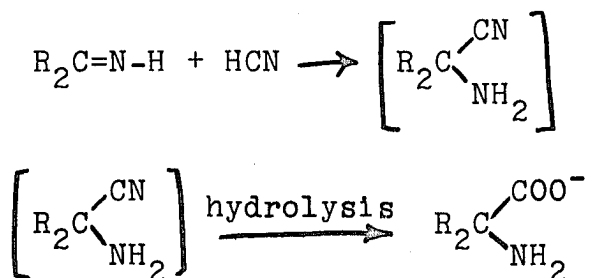
SUGGESTIONS FOR FURTHER WORK

The reaction between imine + CS₂ and copper should make an interesting study. The 2013 cm⁻¹ band observed by Loudon should be of interest here. The explanation of the mechanism of oxidation of the copper and determination of the structure of metal chelates is a challenging problem.

The kinetics and mechanisms of the reaction between the imine and H₂S would be a problem worthy of further investigation. Curve "f" of Figure 13 shows shift toward TMS of the peak initially assigned as =N-H. This shift is quite rapid and increases with addition of very small amounts of H₂S. Curve "d" shows a typical downfield shift in protonations of the imine. Since the effect of H₂S is in the other direction, it seems reasonable to presume that H₂S reacts with imine primarily in some other manner than by protonation. Possibly H₂S adds across the C=N bond:



Thioketone is an observed product of the reaction. The intermediate addition product proposed above is somewhat analogous to that formed in the well known synthesis of α-amino acids:



In a single probing experiment, 0.2823 g imine was dissolved in 25.0 ml CS₂ and H₂S was passed through it at room temperature. The concentration of H₂S was essentially constant, because the system was saturated with H₂S for this experiment. No attempt was made to determine consumption of H₂S. The imine-CS₂ reaction goes very slowly at room temperature, and it was ignored over the relatively short time given the imine-H₂S reaction. Imine and thioketone were determined by the analytical methods in the imine-CS₂ study. Results are given in Table VIII.

TABLE VIII

Results of Analyses Performed on H₂S + Imine
Reaction in CS₂ at 25°C (± 3°C)

Time elapsed (min)	10 ³ x moles imine disappeared	10 ³ x moles thioketone formed	10 ³ x [moles imine disappeared - moles thioketone formed]
0	0.000	0.001	-
52	0.858	0.685	0.173
160	1.066	0.846	0.220
296	1.104	0.836	0.268

More than half the imine disappeared in a relatively short time with about 80% of it accounted for in the production of thioketone. Resolution of the question of whether the other 20% of imine is tied up in an intermediate or consumed in a competing reaction such as protonation should prove an interesting study.

The apparent lability of the imine proton and the large observed NMR shifts in both directions in Figure 15 indicate need for an interesting study. Use of the imine proton as a probe in pH studies on non-aqueous systems could result from a study yielding correlation of NMR shifts with reactions resulting in various changes in the electron density about the imine functional group. The employment of simpler systems than either the imine-CS₂ or imine-H₂S reaction systems is suggested for preliminary work. Use of non-reacting, two-component systems should give proton exchange peak shift data necessary to the interpretation of shifts observed in more complicated reaction systems.

The thioketone, 4,4'-dimethoxythiobenzophenone, (I), produced in the imine-CS₂ and imine-H₂S reactions is an interesting compound. This worker has observed that exposure to sunlight through glass of a 10⁻³ M solution of this thioketone in CCl₄, benzene, or other solvents causes disappearance of the blue color within minutes. The same experiment using 4,4'-dimethylthiobenzophenone, (II), results in stability of the blue color. The methoxy groups of I donate electrons to the ring conjugation system to a

greater extent than the methyl groups of II. Interesting information should result from a study of several selected aryl thioketones with various substituents in the p-position. Determination of the wavelength of exciting light at which the blue color (absorbance at 590 m μ) begins to disappear could lead to the development of several compounds of selective light sensitivity. Since the photochemical reaction may be expected to produce free radicals, these compounds could be used as selective photosensitized initiators in free-radical polymerization processes.

SELECTED BIBLIOGRAPHY

1. Cotton, F. A. and G. Wilkinson
Advanced Inorganic Chemistry
New York: Interscience Publishers, 1962.
2. Donle, H. L. and G. Volkert
"Dipolmomenten and Ultraviolet Absorption Organisher Molekule"
Zeitschrift fur Physikalische Chemie Abteilung, B,
VIII (1930), 60.
3. Feigl, F.
Chemistry of Specific, Selective, and Sensitive Reactions
New York: Academic Press Inc., 1949.
4. Gatterman, L.
"Ueber Gefarbte Aromatische Thioketone"
Berichte, XXVIII (1895), 2869.
5. Huddleston, G. R.
The Kinetics and Mechanism of the Reaction Between Sulfur and N-(4,4'-Dimethoxybenzohydrilidene)benzylamine
A Dissertation. Louisiana State University (1960)
6. Losach, N. and G. Guillouzo
"Sulfuration des Composés Organiques (XI)"
Bull. Soc. Chim. France, (1957), 1221
7. Meche, R. et al
Z. Naturforsch., 10b, (1955), 367.
8. Neely, W. C. and H. B. Williams
"The Reaction of Schonberg's Reagent with Elemental Sulfur"
Anal. Chim. Acta, XXIV (1961), 575.
9. Ory, H. A., V. L. Warren and H. B. Williams
"A Direct Colorimetric Determination of Elementary Sulfur"
The Analyst, LXXXII (1957), 189.
10. Schönberg, A., O. Schutz and S. Nickel
"Darstellung Aromatischer Thio-ketone durch Einwirkung von Thioessigsäure auf Ketochloride"
Berichte, LXI (1928), 1375.

11. Schönberg, A. and W. Urban
"Über eine mikro-chemische Farbreaktion auf Elementaren Schwefel"
Berichte, LXVII (1934), 1999.
12. Williams, H. B., F. M. Hilburn and K. Yarbrough
"Synthesis and Spectral Characteristics of
4,4'-Dimethoxythiobenzophenone"
Anal. Chim. Acta, XXXI (1964), 488.
13. Williams, H. B., P. Koenig, G. Huddleston, T. Couvillon
and W. Castille
"Further Studies of Schonberg's Reagent and Sulfur"
Journal of Organic Chemistry, XXVIII (1963), 463.

VITA

Kenneth Norman Yarbrough was born in Novice, Texas, on March 12, 1932. He attended West Ward Elementary School in Coleman, Texas through eighth grade and was graduated from Paschal High School, Fort Worth, Texas, in May, 1949. He entered North Texas State University, Denton, Texas, in the fall of 1949, and was awarded a Bachelor of Science degree in the spring of 1953. He remained at North Texas State University to receive a Master of Science degree in the summer of 1954, and was subsequently employed there as instructor of chemistry until the fall of 1955. In September of 1955 he accepted a faculty position at Lamar State College of Technology, Beaumont, Texas, where he remained until the spring of 1960. He then spent one year teaching at Texas Technological College, Lubbock, Texas. The first two of the seven years of teaching were spent at the rank of instructor and the last five of these years were spent at the rank of assistant professor. Concurrent with teaching at Lamar, he served three years as city chemist in Beaumont. Four of the seven summers were spent in industry working on special problems; three of the summers were spent in teaching. He entered the graduate school of Louisiana State University in September, 1961, in the Department of Chemistry. He is an associate member of the Society of Sigma Xi. At present he is a candidate for the degree of Doctor of Philosophy.

EXAMINATION AND THESIS REPORT

Candidate: Kenneth Norman Yarbrough

Major Field: Chemistry

Title of Thesis: The Kinetics and Mechanism of the Reaction between Carbon Disulfide and Bis-(p-Methoxyphenyl) Methyleneimine.

Approved:

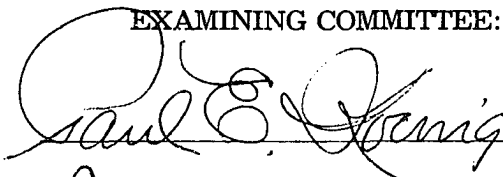


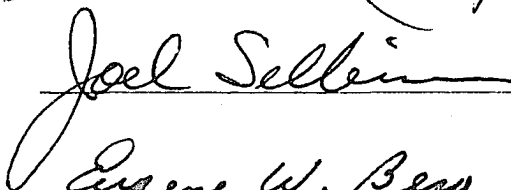
Major Professor and Chairman

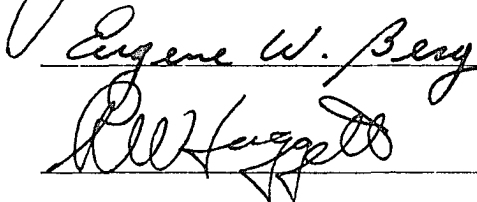


Dean of the Graduate School

EXAMINING COMMITTEE:









Date of Examination:

May 28, 1965